

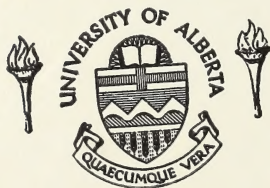
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VAPOUR-LIQUID EQUILIBRIA IN A QUATERNARY
NATURAL GAS SYSTEM

BY

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A THESIS

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ABSTRACT

A review of the results published for systems containing hydrogen sulphide, carbon dioxide, methane, nitrogen, and natural gas is presented. The progress of the concept of vapour-liquid equilibrium is studied with a brief discussion on the methods of correlation and theoretical prediction of the vapour-liquid equilibrium data.

The equilibrium cell was tested for its performance on multicomponent systems. Some modifications were incorporated and a change in the design of the piston is suggested.

The two phase envelope of the quaternary natural gas system containing hydrogen sulphide, carbon dioxide, methane, and nitrogen was defined by measuring percent liquid present for different pressures at nine temperatures, 35°, 60°, 90°, 120°, 140°, 150°, 160°, 170°, and 180°F over a range of pressures from 246 to 1,945 psia. The phenomenon of critical opalescence was observed. A comparison is made with the observations reported by other authors. A photograph showing critical opalescence is presented.

Equilibrium ratios for hydrogen sulphide, carbon dioxide and methane were calculated at 120°F. These values were compared with those presented by three other authors on allied systems. The K-values for methane and carbon dioxide compare reasonably well, but larger discrepancies were observed for the hydrogen sulphide K-values.

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A. INTRODUCTION

A knowledge of the composition and amounts of the coexisting phases under heterogeneous equilibrium and the ability to determine the thermodynamic properties of fluids is basic for most convenient and economic use of the available resources.

Souders, Selheimer, and Brown⁽¹⁶⁶⁾, developed the concept of 'equilibrium constants', and it has been found to be a suitable measure of the vapourization characteristics of petroleum mixtures⁽⁶⁵⁾.

They arbitrarily defined the equilibrium constant K , as the ratio of the mole fraction of a constituent in the vapour phase, y , to the mole fraction of that constituent in the liquid phase, x , at a defined temperature and pressure of the equilibrium. Therefore, at equilibrium

$$K_i = y_i/x_i, \quad y_i = K_i x_i \quad (1)$$

Equilibrium constants are functions of temperature, pressure, and the overall composition of the system. The effect of compositions is very small at low pressures, but, above about 1,000 psia, the equilibrium constants depend considerably on the overall composition of the system⁽¹⁶⁷⁾. The term constant is thus a misnomer, but it is used widely

in the petroleum industry. Muskat⁽¹⁰⁷⁾ has proposed the term 'Equilibrium Ratio'.

Non-hydrocarbons such as hydrogen sulphide, carbon dioxide and nitrogen are important components of the fluids produced from underground petroleum reservoirs. Most binary systems containing paraffin hydrocarbons and some ternary and more complex systems have been investigated. Methods for correlating and predicting such data are available. However, the information available on systems of hydrocarbons and non-hydrocarbons such as hydrogen sulphide and carbon dioxide is very scanty. These systems, in general, exhibit a highly non-ideal behaviour.

The equilibrium cell used in this work was constructed at the University of Alberta in 1961. Sandercock⁽¹⁵⁸⁾ has presented a detailed description of the cell. Hughes⁽⁶⁰⁾ used the cell to study the phase behaviour of the binary system hydrogen sulphide-butane.

The purpose of this investigation was:

- (1) to assess the performance of the existing equipment with a multicomponent system and to modify it, if necessary.
- (2) to design a convenient unit for making multicomponent gas samples of any desired composition.

- (3) to employ the equipment in the study of the phase behaviour of a natural gas system at a series of suitable pressure and temperatures.
- (4) to compare the equilibrium ratios thus obtained with values reported in the literature on related systems.

B. THEORY

(1) Literature Review

The vapour pressures of hydrogen sulphide were reported by West⁽¹⁸⁵⁾. Reamer, Sage, and Lacey⁽¹²¹⁾ presented data on its phase and volumetric behaviour. Data on several binary systems containing hydrogen sulphide have been reported. The phase and volumetric behaviour of the system methane - hydrogen sulphide was reported by Reamer, Sage, Lacey⁽¹²²⁾. They studied the system at temperatures ranging from 40 to 340°F and pressures up to 10,000 psia. Kohn and Kurata⁽⁷⁸⁾ studied this system for the temperature range of -300 to 300°F and pressures up to 2,000 psia and thus extended the data to lower temperatures. They report the existence of type K singular points for this system where two phases are in critical identity in the presence of a third phase. This system did not exhibit any azeotropic behaviour for the whole range of temperatures investigated.

Kay and Brice⁽⁶⁷⁾ reported the system ethane-hydrogen sulphide for the temperature range of -7 to 212°F and pressures up to 1,200 psia. A minimum boiling azeotrope was observed at concentrations high in ethane and persisted up to the

critical point. The phase equilibrium data for the system hydrogen sulphide - propane were investigated by Kay and Rambosek⁽⁶⁸⁾ from 32°F to the critical locus. Brewer, Rodewald and Kurata⁽³²⁾ extended the data on this system to the solid - liquid - vapour region which starts about -125°F. They studied this system for the temperature range of -130 to 140°F and verified the data of previous authors in the region common to both the investigations. Steckel⁽¹⁶⁹⁾ has studied this system in the temperature range of -30 to 15°C while Gilliland and Scheeline⁽⁵⁴⁾ restricted their investigation to the temperature range of 124 to 201°F and pressures between 400 and 600 psia. In this system, an azeotrope was formed at high hydrogen sulphide concentrations and persisted up to the critical region.

Sandercock⁽¹⁵⁸⁾ studied the phase behaviour of the system hydrogen sulphide - butane at 100°F and Hughes⁽⁶⁰⁾ has reported data in the temperature range of 125 to 275°F and pressures up to 1,780 psia. No actual azeotrope was observed but his data indicate a tendency toward an azeotropic behaviour.

Reamer, Sage, and Lacey⁽¹²³⁾ studied the phase and volumetric behaviour of the system pentane - hydrogen sulphide in the temperature range of 40 - 460°F and for pressures up to 10,000 psia. No azeotrope was formed. The phase and volumetric

behaviour of the system hydrogen sulphide - decane was reported by Reamer, Selleck, Sage, and Lacey⁽¹²⁴⁾ at temperatures ranging from 40 - 460°F and for pressures up to 10,000 psia. They found the system to be of the common binary type with no unusual behaviour.

The hydrogen sulphide - carbon dioxide binary has been studied by Bierlein and Kay^(23,24) from 0°C to the critical point of hydrogen sulphide. The system exhibited a tendency to form a minimum boiling azeotrope, but no actual azeotrope is reported. Steckel⁽¹⁶⁹⁾ has reported isothermal dew and bubble point pressures for this system at 0°, -26.8°, and -52°C. His results at 0°C, though qualitatively similar differ somewhat quantitatively from those of Bierlein and Kay. Kurata and Sobocinski⁽⁸⁷⁾ investigated this system from the critical region to the solid-liquid-vapour region.

Robinson et al^(139, 140) investigated the methane - carbon dioxide - hydrogen sulphide ternary. These investigators reported equilibrium constants for each component as a function of pressure and ratio of other components at 100°F, 50°F, and 160°F and at pressures up to 1,600 psia.

Very recently Cramer⁽⁴²⁾ has compiled the phase diagrams for carbon dioxide up to 12,000 atmospheres. Kuenan⁽⁸³⁻⁸⁶⁾ was perhaps the first to investigate the behaviour of paraffin

hydrocarbons and carbon dioxide. His measurements indicated a minimum boiling azeotropic behaviour for the system ethane - carbon dioxide. Sweigert⁽¹⁷²⁾ has compiled the thermodynamic properties of carbon dioxide in the temperature range of -75 to 1,800°F and for pressures up to 3,000 psia.

Reamer, Olds, Sage and Lacey⁽¹²⁵⁾ investigated the system methane - carbon dioxide in the gaseous region at temperatures ranging from 100° to 460°F and throughout the pressure interval from 100 to 10,000 psia. Donnelly and Katz^(47,48) have reported the solid-liquid-vapour equilibrium data for this system in the temperature range of -100 to 29°F and for pressures up to 1,150 psia.

The volumetric behaviour for the system ethane - carbon dioxide has been reported by Reamer, Olds, Sage, and Lacey⁽¹²⁶⁾ at temperatures ranging from 100 - 460°F and for pressures up to 10,000 psia.

Poettman and Katz⁽¹¹⁸⁾ reviewed the literature relating to binary mixtures of carbon dioxide and hydrocarbons. In addition, they studied the phase behaviour of mixtures of carbon dioxide with propane, butane, and pentane. They investigated the system propane - carbon dioxide at temperatures ranging from 32 to 210°F and for pressures up to 1,000 psia, the system butane - carbon dioxide in the temperature range

of 45 to 300°F and for pressure up to 1,180 psia, and the system pentane - carbon dioxide at temperatures between 45 and 365°F and for pressures up to 1,450 psia.

Reamer, Sage, and Lacey⁽¹²⁷⁾ presented data on the volumetric behaviour of the system carbon dioxide - propane at temperatures ranging from 40 to 460°F and pressures up to 10,000 psia. They studied the vapour-liquid equilibrium of this system in the temperature range of 40 to 160°F and for pressures up to 1,002 psia. Akers, Kelley, and Lipscomb⁽¹⁾ worked at lower temperatures between -40 and 32°F and for pressures up to 507 psia. The critical locus of this system shows a sharp downward curvature at the carbon dioxide end of the line, thereby indicating that the forces tending to form a minimum boiling azeotrope as in the ethane - carbon dioxide system have not yet completely disappeared.

Olds, Reamer, Sage and Lacey⁽¹⁰⁹⁾ investigated volumetric behaviour of the system butane - carbon dioxide at temperatures between 100 and 460°F and for pressures up to 10,000 psia. They also reported data on the vapour-liquid equilibrium of this system in the temperature interval 100 - 280°F and for pressures up to 1,200 psia. This system also exhibited a reversal in the curvature of the bubble point pressure-composition relationships.

Mathews and Hurd⁽⁹⁹⁾ in 1946 utilized the data of Kvalnes and Gaddy⁽⁸⁸⁾ and Olds, Reamer, Sage, and Lacey⁽¹¹⁰⁾ to establish the P-V-T behaviour of methane in the superheated region. They also used the data of Keyes, Taylor, and Smith⁽⁷⁶⁾ on the saturated liquid densities of methane in conjunction with the Clapeyron equation to develop the densities for the saturated envelope. This enabled them to establish densities up to $P_r = 20$. The data of Schamp, Mason, Richardson, and Altman⁽¹⁶¹⁾, Michels and Nederbragt^(104,105), Keyes and Burke⁽⁷⁴⁾, Keyes, Smith, and Joubart⁽⁷⁵⁾, and those of Amagat^(6,7) reinforce the information resulting from the data of Olds, Reamer, Sage, and Lacey and Kvalnes and Gaddy in the intermediate to high pressure region. The data of Kazarnovskii and Levchenko⁽⁶⁹⁾ extended the high pressure data of Olds et al to temperatures up to $T_r = 3.08$. Matschke and Thodos⁽¹⁰⁰⁾ calculated the densities of compressed liquid methane up to pressures of $P_r = 20$ and temperatures as low as $T_r = 0.5$.

The system methane - ethane has been investigated by Ruhemann⁽¹⁴⁷⁾ in the temperature range from -104 to 0°C and pressures up to 100 atmospheres. At pressures below 15 atmospheres, the system behaved nearly ideally obeying the perfect solution laws.

Sage, Lacey, and Schaafsma⁽¹⁴⁹⁾ investigated the system methane - propane at temperatures between 20 to 90°C and pressures up to 200 atmospheres. The system was found to have a large region of retrograde condensation of the first kind. Akers, Burns, and Fairchild⁽²⁾ extended the data on the system to lower temperatures ranging between -176 to 32°F and for pressures up to 1,450 psia.

The system butane - methane has been studied extensively by various authors^(108,128,150,151,137). The combined data of these investigators embraced the range of temperatures from -4° to 460°F and pressures from 147 to 10,000 psia.

Sage, Reamer, Olds, and Lacey⁽¹⁵³⁾ have investigated the phase and volumetric behaviour of the system methane - pentane at temperatures ranging from 100 to 400°F and for pressures up to 5,000 psia.

The methane - decane system has been investigated over a wide range of temperatures from 70 - 460°F and for pressures up to 10,000 psia^(152,90,153).

Volumetric measurements on nitrogen have been reported for temperatures from 0 to 800°F at pressures from atmospheric to 15,000 psia^(13,190,114,59,8,102,103,61). Sage and Lacey⁽¹⁵⁴⁾ and Bloomer and Rao⁽³⁰⁾ have tabulated the thermodynamic properties of nitrogen.

Akers, Attwell, and Robinson⁽⁴⁾ have investigated the system nitrogen - butane. The system nitrogen - heptane was reported by Akers, Kehn, and Kilgore⁽³⁾. Some data are available for the system nitrogen - carbon dioxide at 0°C and for pressures up to 7,000 psia⁽¹⁷⁸⁾.

Various investigators have reported data on systems containing a natural gas and hydrocarbon liquids such as crude oil, absorption oil, and gas distillate. In some cases, they have reported the equilibrium ratios for components such as hydrogen sulphide, carbon dioxide, methane, and nitrogen.

The systems containing hydrogen sulphide, carbon dioxide, methane, nitrogen, and natural gas on which data are available are summarized in tables 1 to 5 respectively.

Table No. 1

REFERENCES ON HYDROGEN SULPHIDE SYSTEMS

<u>System</u>	<u>Authors</u>	<u>Citation</u>
1. $\text{CH}_4\text{-H}_2\text{S}$	Reamer, Sage, and Lacey Kohn and Kurata	122 78
2. $\text{C}_2\text{H}_6\text{-H}_2\text{S}$	Kay and Brice	67
3. $\text{C}_3\text{H}_8\text{-H}_2\text{S}$	Kay and Rambosek Brewer, Rodewald, and Kurata Gilliland and Scheeline Steckel	68 32 54 169
4. $\text{C}_4\text{H}_{10}\text{-H}_2\text{S}$	Hughes Sandercock	60 158
5. $\text{n-C}_5\text{H}_{12}\text{-H}_2\text{S}$	Reamer, Sage, and Lacey	123
6. $\text{n-C}_{10}\text{H}_{22}\text{-H}_2\text{S}$	Reamer, Selleck, Sage, and Lacey	124
7. $\text{C}_3\text{H}_6\text{-H}_2\text{S}$	Steckel	169
8. $\text{H}_2\text{S-CO}_2$	Bierlein and Kay Kurata and Sobocinski Steckel	23,24 87 169
9. $\text{H}_2\text{S-CH}_4\text{-CO}_2$	Robinson, Lorenzo, and Macrygeorgos Robinson and Bailey Kennedy and Wieland	139 140 73
10. $\text{H}_2\text{S-H}_2\text{O}$	Selleck, Carmichael, and Sage	163
11. $\text{H}_2\text{S-H}_2\text{O-ethanolamine}$	Atwood, Arnold, and Kindrick	12
12. $\text{H}_2\text{S-Reservoir fluid}$	Vagtborg	181

Table No. 2

REFERENCES ON CARBON DIOXIDE SYSTEMS

<u>System</u>	<u>Authors</u>	<u>Citation</u>
1. C ₁ -CO ₂	Donnelly and Katz Reamer, Olds, Sage, and Lacey Tsikilis	47, 48 125 178
2. C ₂ -CO ₂	Reamer, Olds, Sage, and Lacey Kuenan	126 83 - 86
3. C ₃ -CO ₂	Akers, Kelley, and Lipscomb Reamer, Sage, and Lacey Poettman and Katz	1 127 118
4. C ₄ -CO ₂	Poettman and Katz Olds, Reamer, Sage, and Lacey	118 109
5. C ₅ -CO ₂	Poettman and Katz	118
6. H ₂ S-CO ₂	Bierlein and Kay Kurata and Sobocinski Steckel Thiel and Schulte	23, 24 87 169 174
7. CH ₄ -CO ₂ -H ₂ S	Robinson, Lorenzo, and Macrygeorgos Robinson and Bailey Kennedy and Wieland	140 139 73
8. C ₂ H ₂ -CO ₂	Kuenan	84
9. C ₂ H ₄ -CO ₂	Tsikilis	179
10. (C ₂ H ₅) ₂ O-CO ₂	Thiel and Schulte	174
11. CO ₂ -SO ₂	Caubet Thiel and Schulte	40 174
12. CO ₂ -Natural Gas- Condensate	Poettmann and Katz	116
13. CO ₂ -Natural Gas- Crude Oil	Poettman	117

Table No. 2 (Continued)

14.	$\text{CO}_2\text{-N}_2$	Tsikilis Torocheshnikov Andrews	178 175 10
15.	$\text{C}_2\text{H}_5\text{Cl-CO}_2$	Thiel and Schulte	174
16.	$\text{CO}_2\text{-Cl}_2$	Thiel and Schulte	174
17.	$\text{CO}_2\text{-(CH}_3)_2\text{O}$	Thiel and Schulte	174
18.	$\text{CO}_2\text{-air}$	Cailletet Van der Waals	36 182
19.	$\text{CO}_2\text{-H}_2$	Vershafield	183
20.	$\text{CO}_2\text{-HCl}$	Ansdell	11
21.	$\text{CO}_2\text{-CH}_3\text{Cl}$	Kuenan Caubet	83, 86 39
22.	$\text{CO}_2\text{-N}_2\text{O}$	Caubet	39
23.	$\text{CO}_2\text{-C}_6\text{H}_5\text{NO}_2$	Kohnstamm and Reeder	79
24.	$\text{CO}_2\text{-O}_2$	Keesom	70 - 72

Table No. 3

REFERENCES FOR METHANE SYSTEMS

<u>System</u>	<u>Authors</u>	<u>Citation</u>
1. $\text{CH}_4\text{-C}_2\text{H}_6$	Ruhemann Bloomer, Gami, and Parent	147 29
2. $\text{CH}_4\text{-C}_3\text{H}_8$	Sage, Lacey, and Schaafasma Reamer, Sage, and Lacey Akers, Burns, and Fairchild	149 134 2
3. $\text{CH}_4\text{-n-C}_4\text{H}_{10}$	Neberbraght Reamer, Korpi, Sage, and Lacey Sage, Budenholzer, and Lacey Sage, Hicks, and Lacey Rigas, Mason, and Thodos	108 128 150 151 137
4. $\text{CH}_4\text{-i-C}_4\text{H}_{10}$	Olds, Sage, and Lacey	111
5. $\text{CH}_4\text{-n-C}_5\text{H}_{12}$	Sage, Reamer, Olds, and Lacey Taylor, Wald, Sage, and Lacey Boomer, and Johnson	153 173 31
6. $\text{CH}_4\text{-i-C}_5\text{H}_{12}$	Amick, Johnson, and Dodge	9
7. $\text{CH}_4\text{-hexanes}$	Boomer and Johnson	31
8. $\text{CH}_4\text{-nC}_7\text{H}_{16}$	Boomer and Johnson Reamer, Sage, and Lacey	31 129
9. $\text{CH}_4\text{-nC}_{10}\text{H}_{22}$	Sage, Lavender, and Lacey Reamer, Olds, Sage, and Lacey	152 153
10. $\text{CH}_4\text{-C}_2\text{H}_6\text{-C}_2\text{H}_4$	Guter, Newitt, and Ruhemann	56
11. $\text{CH}_4\text{-C}_2\text{H}_4$	Guter, Newitt, and Ruhemann	56
12. $\text{CH}_4\text{-C}_3\text{H}_8\text{-nC}_4\text{H}_{10}$	Rigas, Mason, and Thodos	138
13. $\text{CH}_4\text{-nC}_4\text{H}_{10}\text{-nC}_{10}\text{H}_{22}$	Reamer, Fiskin, and Sage Reamer, Sage, and Lacey	130 131-133

14.	$\text{CH}_4\text{-nC}_4\text{H}_{10}\text{-H}_2\text{O}$	McKetta and Katz	101
15.	$\text{CH}_4\text{-H}_2\text{O}$	Olds, Sage, and Lacey	112
16.	$\text{CH}_4\text{-N}_2\text{-Cyclohexane}$	Johnson	64
17.	$\text{CH}_4\text{-N}_2\text{-Heptane}$	Johnson	64
18.	$\text{CH}_4\text{-N}_2\text{-Benzene}$	Johnson	64
19.	$\text{CH}_4\text{-N}_2\text{-Toluene}$	Johnson	64
20.	$\text{CH}_4\text{-Crystal Oil}$	Sage, Backus, and Lacey	155
21.	$\text{CH}_4\text{-Kensol-16}$	Rzasa	148
22.	$\text{CH}_4\text{-CO}_2$	Donnelly and Katz Reamer, Olds, Sage, and Lacey Tsikilis	47, 48 125 178
23.	$\text{CH}_4\text{-H}_2\text{S}$	Reamer, Sage, and Lacey Kohn and Kurata	122 78
24.	$\text{CH}_4\text{-CO}_2\text{-H}_2\text{S}$	Robinson, Lorenzo, and Macrygeorgos Robinson and Bailey Kennedy and Wieland	140 139 73
25.	$\text{CH}_4\text{-NH}_3$	Krichevsky and Tsikilis	80
26.	$\text{CH}_4\text{-CO}$	Toyama	176
27.	$\text{CH}_4\text{-Crude Oil-}$ Natural Gas	Buckley	34
28.	$\text{CH}_4\text{-Natural Gas}$	Davis, Bertuzzi, Gore, and Kurata	45
29.	$\text{CH}_4\text{-Crude Oil}$	Sage, Webster, and Lacey	156

Table No. 4

REFERENCES ON NITROGEN SYSTEMS

<u>System</u>	<u>Authors</u>	<u>Citation</u>
1. $N_2-nC_4H_{10}$	Akers, Attwell, and Robinson	4
2. $N_2-nC_7H_{16}$	Akers, Kehn, and Kilgore	3
3. N_2-CO_2	Tsikilis Torochoeshnikov Andrews	178 175 10
4. $N_2-CO_2-O_2$	Zenner and Dana	196
5. N_2-CO	Schiller and Canjar	162
6. $N_2-C_2H_4$	Tsikilis	179
7. N_2-H_2O	Bassett and Dodge	14
8. N_2-SO_2	Tsikilis	180
9. N_2 -Benzene	Krishchevsky	82
10. N_2-NH_3	Wiebe and Gaddy Krishchevsky and Tsikilis Lindroos and Dodge Krishchevsky and Bolshakov	189 80 96 81
11. N_2 -Natural Gas	Davis, Bertuzzi, Gore, and Kurata	45
12. N_2-He	Buzyna, Macriss, and Ellington	35
13. N_2-A	Long and DiPaolo	97

Table No. 5

REFERENCES ON NATURAL GAS SYSTEMS

<u>System</u>	<u>Authors</u>	<u>Citation</u>
1. Natural gas	Gore, Davis, and Kurata Brown and Stutzman	55 33
2. Natural gas- distillate	Poettman and Katz Roland, Smith, and Kaveler	116 145
3. H ₂ S-CO ₂ -Natural Gas	Robinson, Macrygeorgos and Govier	141
4. nC ₇ H ₁₆ -Natural Gas	Boomer, Johnson, and Piercey	31
5. Natural gas-N ₂ or CH ₄	Davis, Bertuzzi, Gore and Kurata	45
6. CO ₂ -Natural gas- Crude Oil	Poettman Roland	117 144
7. CH ₄ -Natural Gas- Crude Oil	Buckley	34
8. Natural gas-Crude Oil	Katz and Hachmuth Standing and Katz Jacoby and Rzasa	65 168 62
9. Natural gas- Absorption Oil	Kirkbride and Bertetti Jacoby and Rzasa	77 63
10. Natural Gas-Natural Gasoline	Katz and Kurata	66
11. Multicomponent hydrocarbon systems	Sage and Lacey	154
12. Hydrocarbons in Absorption Oil	Webber	184

(2) Phase Behavior Principles

Equilibrium in a close system implies a situation in which there is no change with respect to time. If we consider a 2-phase system at equilibrium containing n components and concern ourselves with the mole fraction y_i of the i^{th} component in the vapour phase and x_i of the same component in the liquid phase, the equilibrium ratio for this component is arbitrarily defined as

$$K_i = y_i/x_i \quad (1)$$

The definition of "ideal equilibrium ratios" comes from the concept of a "perfect solution". If the molecules of the components of the solution are so similar that the forces between unlike molecules are the same as those between like molecules and if the components mix without the complicating effects of molecular association or chemical combination the solution would obey Raoult's Law⁽¹²⁰⁾,

$$P_i = x_i P_{vi} \quad (2)$$

where,

P_i is the partial pressure of the i^{th} component over the solution, and

P_{vi} is the vapour pressure of the i^{th} component in its pure state at the same temperature.

Dalton's Law⁽⁴⁴⁾ states that the total pressure of a gas is equal to the sum of the partial pressures of the components present, thus

$$P_i = y_i P \quad (3)$$

where,

P is the total pressure of the system.

Equations (2) and (3) may be combined to give,

$$K_i = y_i/x_i = \frac{P_{vi}}{P} \quad (4)$$

This equation suggests a useful method of representing the equilibrium ratios graphically. Taking logarithms of both sides of equation (4), one obtains

$$\log K_i = \log P_{vi} - \log P \quad (5)$$

Hence a log-log plot of K_i versus P will give a straight line having a slope of -1, passing through $K_i = 1$ where $P = P_{vi}$ at the temperature in question.

It has been shown that Raoult's and Dalton's Laws are not exact even in relatively simple mixtures of hydrocarbons (37,142,192).

In general, K-factors predicted by this method are restricted to low pressures, some considerable distance from the critical pressure and to ideal solutions. Normal paraffin

hydrocarbons form ideal solutions over certain ranges of pressure and temperature⁽¹⁴³⁾, but the presence of components such as water, hydrogen, carbon dioxide, hydrogen sulphide, or olefins frequently cause significant deviations.

G.N. Lewis⁽⁹⁵⁾ proposed the use of fugacity in place of pressure whenever the fluids behave non-ideally. A closer approximation to actual k-factors is obtained if partial pressure and pressure are replaced by fugacities in making equilibrium calculations. An ideal solution is defined as one in which the fugacity of each component is proportional to the mole fraction of that component at every temperature and pressure⁽⁹⁴⁾. The equilibrium ratios defined in terms of fugacity are sometimes called 'ideal solution equilibrium ratios'.

Defining the fugacity at constant temperature T, as

$$d \ln f = v dp \quad (6)$$

where,

f is the fugacity, v is the molal volume of vapour, and p the partial pressure of the component. The Dalton's Law type equation becomes,

$$\bar{f}_i^v = y_i f_i^v \quad (7)$$

and the Raoult law type equation becomes

$$\bar{f}_i^L = x_i f_i^L \quad (8)$$

where, a bar denotes the fugacity of component in the mixture, v and L stand for vapour and liquid respectively.

The criteria for equilibrium, which are

$$T^V = T^L, p^V = p^L, \text{ and } \bar{f}_i^V = \bar{f}_i^L \quad (9)$$

give

$$K_{ideal} = \frac{y_i}{x_i} = \frac{f_i^L}{f_i^V} \quad (10)$$

In this case, fugacities have replaced the pressure in equation (4). K_{ideal} is a function of system temperature and pressure only and is independent of composition.

Many generalized K-factor correlations based on the fugacity concept have been presented^(20,49,119). These idealized approaches are not truly descriptive and large deviations are encountered in non-ideal systems. Experimental data have shown that the K-factors for any component are functions of the temperature, the pressure, and the composition of the system. Various attempts have been made to devise a suitable parameter to account for the effect of composition.

The K-factors are observed to converge to unity at some pressure for each temperature chosen. This leads to the concept of convergence pressure, which at the present time is generally accepted as the best means available to relate K-factors to composition.

The convergence pressure is defined as the pressure at which K's for all components appear to converge to unity at the system temperature. The K's are actually continuous up to $K=1$ only when the equilibrium temperature happens to be the critical temperature of the system. At temperatures other than the critical, the discontinuous curves on a $\log K$ vs $\log P$ plot when extended appear to converge to unity⁽⁵⁰⁾.

From Gibbs phase rule, for two phase equilibria,

$$K = \phi(P, T, \text{Composition of } (n-2) \text{ components}) \quad (11)$$

where, n is the number of components of the mixture.

If we express,

$$K = \phi'(P, P_{cv}) \quad (12)$$

then

$$P_{cv} = \phi''(T, \text{Composition of } (n-2) \text{ Components}) \quad (13)$$

where, P_{cv} is the convergence pressure of the system. For binary systems the convergence pressure is the critical pressure of the mixture having a critical temperature equal to the system temperature.

The application of convergence pressure to multi-component systems requires treating the multicomponent mixture as a hypothetical binary while estimating the K-factors.

Many methods have been presented to calculate the convergence pressure^(57,95,165) and charts are available^(58,193)

to obtain the equilibrium ratios when the convergence pressure is known.

For mixtures of paraffin hydrocarbons the convergence pressure is found to be a satisfactory parameter to account for the effect of composition. However, the addition of non-hydrocarbons may destroy the usefulness of the convergence pressure type correlations.

Activity coefficients have been used in the case of reasonably ideal systems to extend the vapour-liquid equilibrium data to high pressures^(52,164). Smith and Watson⁽¹⁶⁴⁾ employed high pressure activity coefficients to correlate the vapour-liquid equilibrium data on paraffin hydrocarbons. In the 184 systems they studied an average deviation of 15% was observed. The mean deviation was 216% without the use of activity coefficients.

Normal boiling points have been used as a correlating parameter for the vapour-liquid equilibrium data on paraffin hydrocarbon systems⁽¹¹³⁾ but their application is limited only to such systems.

The techniques available to predict equilibrium ratios are

(i) Raoult's and Dalton's Laws. Their application is limited to systems approximating ideal solutions.

(ii) Cluster theory of vapour-liquid equilibria. Lu, James, and Ting⁽²²⁾ postulated that deviations from the ideal behaviour are due to the formation of clusters in liquid and vapour phases.

By writing equilibrium equations between clusters and molecules of the two components, these authors calculated the vapour-liquid equilibria for binary systems. Assuming the clusters to be formed among three components or more, the above method was extended to calculate the vapour-liquid equilibria for complex systems. Applicability of this theory has not been tested sufficiently so far, particularly so for hydrocarbon - non hydrocarbon systems.

(iii) Activity coefficients. One can define the deviation factors from Raoult's law as follows:

$$\gamma_i = \frac{P y_i}{P_{v_i} x_i} \quad (14)$$

The term introduced as a deviation factor from Raoult's law can be shown to be equivalent to the thermodynamic property, activity coefficient.

Lewis and Randall⁽⁹⁴⁾ defined activity, as the relative fugacity, or the ratio between fugacity of the substance in solution and its fugacity at a standard state. Thus, for pure liquid as the standard state:

$$a_i = \frac{f_i}{f_i^L} \quad (15)$$

Activity coefficients are simply the activities divided by their respective mole fractions of $\gamma_i = \frac{a_i}{x_i}$, Thus:

$$\gamma_i = \frac{f_i}{f_i^L x_i} \quad (16)$$

Where the vapours are perfect gases, $f_i = p_i$ and $f_i^L = p_{vi}$, so that

$$\gamma_i = \frac{p_i}{p_{vi} x_i} = \frac{p y_i}{p_{vi} x_i}$$

It is thus apparent that the deviation factors defined by equation (14) are equivalent to values of activity coefficients under conditions that the vapours approximate perfect gases.

A number of methods have been proposed for predicting the activity coefficients (21,38,89,98,135,136,159,194) with the objective to permit the evaluation of γ , as a function of liquid phase composition from a minimum of experimental data. These methods are derived from the solutions of the Gibbs'-Duhem equation when expressed in terms of activity coefficients. The most well-known of these solutions are the equations derived by van Laar⁽⁸⁹⁾, Margules⁽⁹⁸⁾, and Scatchard and Hamer⁽¹⁵⁹⁾.

These may be used to calculate vapour-liquid equilibria for non-ideal systems. Only a knowledge of van Laar constants is needed. These equations have been employed in the case of non-associating solutions with considerable success^(5,41,51,53,38,146,186,187,188,21,135,159,160,89,98).

For solutions of associating components, the van Laar equations are generally unsatisfactory. Similarly, with two coefficients the Margules relations are inadequate for most associating systems and particularly binary systems in which activity coefficients for the two components are non-symmetrical. In such cases, the van Laar type equation is usually superior. Margules type equations give better results when more terms are included. Scatchard and Hamer equations have advantages over others in some special cases. They fail, sometimes, due to the lack of accurate data on boiling points as a function of composition at constant pressure. These equations are valid only for constant temperature data. They have not been used for systems containing non-hydrocarbon components such as H_2S or CO_2 .

(iv) Theory of liquid mixtures. Sweeny and Rose⁽¹⁷¹⁾ have developed a very complex method of predicting vapour-liquid equilibria using a theory of liquid mixtures. Its applicability to hydrocarbon systems has not been studied.

(v) Activity coefficients from molecular structure. Deal, et al^(46,115,192) suggested that in any solvent environment, the partial molal excess free energy of solution of a solute molecule can be taken as the sum of individual contributions from each of its structural groupings and that these contri-

butions depend in some way upon the numbers and kinds of structural groupings which make up the environment. No extension of a group approach to excess free energies or activity coefficients has, however, appeared recently.

(vi) The law of corresponding states. The theory of corresponding states was suggested by van der Waals. Its application to multicomponent systems was based on the Lewis-Randall ideal solution rule approximation. The K-factors predicted by this method were thus greatly in error near the critical point of mixtures. Leland et al^(91,92) have recently derived a rigorous definition of pseudocritical temperature and pressure. This new definition is valid for all vapour-liquid compositions and for non-polar substances, even in the critical region of mixture. Toyama⁽¹⁷⁶⁾ employed this method to the CH_4 -CO system. The overall average absolute deviations were 11.98% for CO and 9.27% for CH_4 .

(vii) Modified van Laar equations. Recently, Black^(26,27,28) has developed a new equation of state. Using this equation of state, he has modified the van Laar type of equations. The effect of association and inter-association between the molecules has been accounted for. The vapour-liquid equilibrium of complex systems can be predicted from binary coefficients alone. The equation, however, has not been applied to hydrocarbon - non hydrocarbon systems.

(viii) Equation of State. An empirical equation of state proposed by Benedict, Webb, and Rubin^(15,20) is frequently used to predict the vapour-liquid equilibria. The use of B-W-R equation is based upon the assumptions that

- a. it is applicable to each of the components, to their mixtures, and to both the vapour and the liquid phases.
- b. that the eight constants of the equation are known for the pure components and that the constants for the mixture can be calculated from these values, using the recommended mixture rules. This equation gives satisfactory results for most light hydrocarbon mixtures^(43,162,170,106,176). Results of Toyama⁽¹⁷⁶⁾ indicate that the agreement between the actual and predicted K-factors is poor for hydrocarbon - non hydrocarbon mixtures.

C. EXPERIMENTAL STUDIES

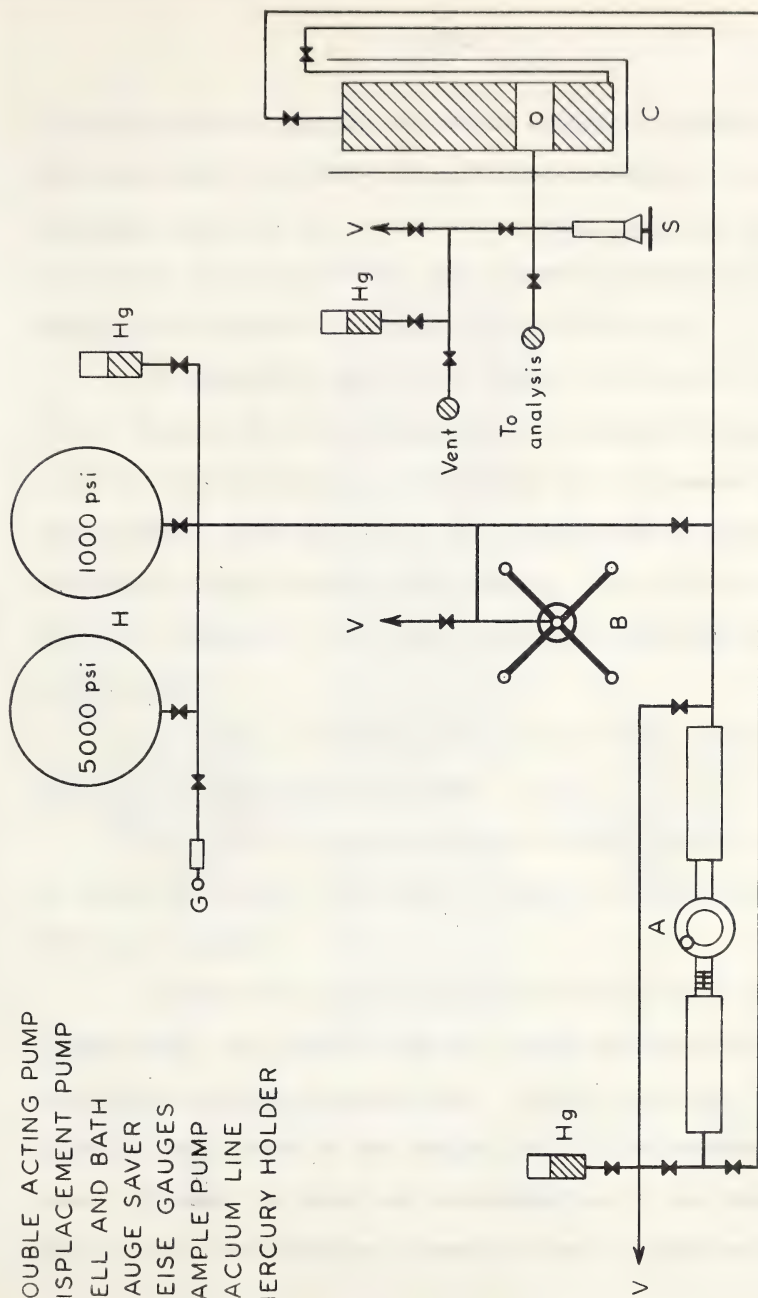
(1) Experimental Apparatus

A very complete and detailed description of the vapour-liquid equilibrium cell was presented by Sandercock⁽¹⁵⁸⁾. Hughes⁽⁶⁰⁾ has reported a few changes in the cell assembly. Basically, it is a windowed cell of variable volume. Some of the outstanding features of this apparatus are:

(1) Position of the vapour-liquid interface can be changed without a change in sample volume. This is accomplished by connecting the top and bottom of the cell respectively to two ends of a double acting pump. This enables removal of mercury from one end of the cell at the same rate that it is added to the other. There is a movable piston at the top of the cell and the sample contained between the piston and the mercury at the bottom can be moved to any desired level in the cell.

(2) The bottom of the cell is also connected to a positive displacement pump and the volume of the sample in the cell can be increased or decreased at will by the withdrawal or addition of mercury to the cell.

(3) The window of the cell is lighted and it can be viewed through a telescope by means of a periscope arrangement.



- A-DOUBLE ACTING PUMP
- B-DISPLACEMENT PUMP
- C-CELL AND BATH
- G-GAUGE SAVER
- H-HEISE GAUGES
- S-SAMPLE PUMP
- V-VACUUM LINE
- Hg-MERCURY HOLDER

FIG.1 SCHEMATIC DIAGRAM OF EQUIPMENT

A pin protruding from the bottom of the piston serves as the reference level for all volumetric measurements. The displacement pump and the double acting pump have been calibrated for volume previously⁽¹⁵⁸⁾. The expected accuracy of volumetric measurements is believed to be ± 0.005 ml.

(4) There is a small port below the window of the cell. Mercury or liquid samples can be sprayed through this port into the gas phase to facilitate the attainment of equilibrium. Some difficulty was encountered in spraying when very small liquid samples were present. In this case, considerable time was required to allow the liquid to drain down the cell after spraying.

(5) Samples are taken from a port at the window level through a calibrated sample pump.

The schematic arrangement of the cell and its accessories is shown in figure 1 and figure 2 shows a section through the cell assembly.

A change was incorporated in the positioning of the sample pump. The sample pump was placed horizontally in the work prior to this investigation. In that position, it was possible for a slug of the sample fluid to be trapped in the pump. In order to avoid any contamination of the samples due to such a possibility it was decided to place the sample

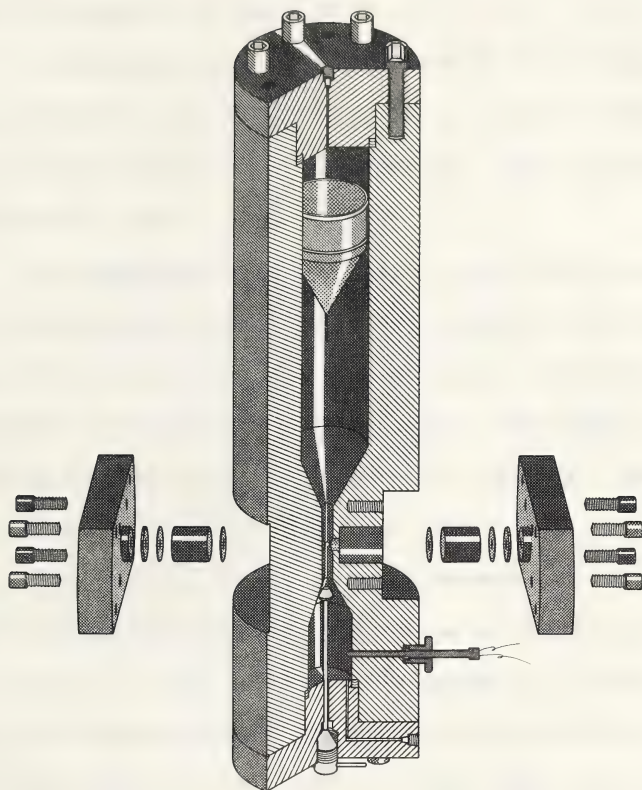


FIGURE 2 ASSEMBLY VIEW OF EQUILIBRIUM CELL

pump vertically. A new pump was constructed which has a micrometer attachment for an accurate measurement of the volume of the samples withdrawn. The detailed drawing of the sample pump is presented in figure 3.

Unlike the previous arrangement^(60,158), only one port is provided for the introduction of any fluid in the cell and also for the withdrawal of the samples. This eliminates some unnecessary lines.

The temperature of the cell was measured by means of an iron-constantan thermocouple and a Leeds and Northrup model K-2 potentiometer. The thermocouple calibration is presented in figure 13 of the appendix. The expected accuracy of temperature measurements is $\pm 0.05^\circ\text{F}$. The temperature of the reference junction was 32°F .

The pressure in the cell was measured by means of two Heise bourdon tube gauges. The rating of these gauges were 1,000 and 5,000 psi, and they were marked at intervals of 2 and 10 psi respectively. The gauges were calibrated by means of a dead weight tester. The 1,000 psi gauge showed no error between the actual pressure and the scale reading for the entire range. In the range of pressures up to 3,000 psi, the maximum error in the scale reading of the 5,000 psi gauge was less than ± 2 psi. A constant correction was applied for the

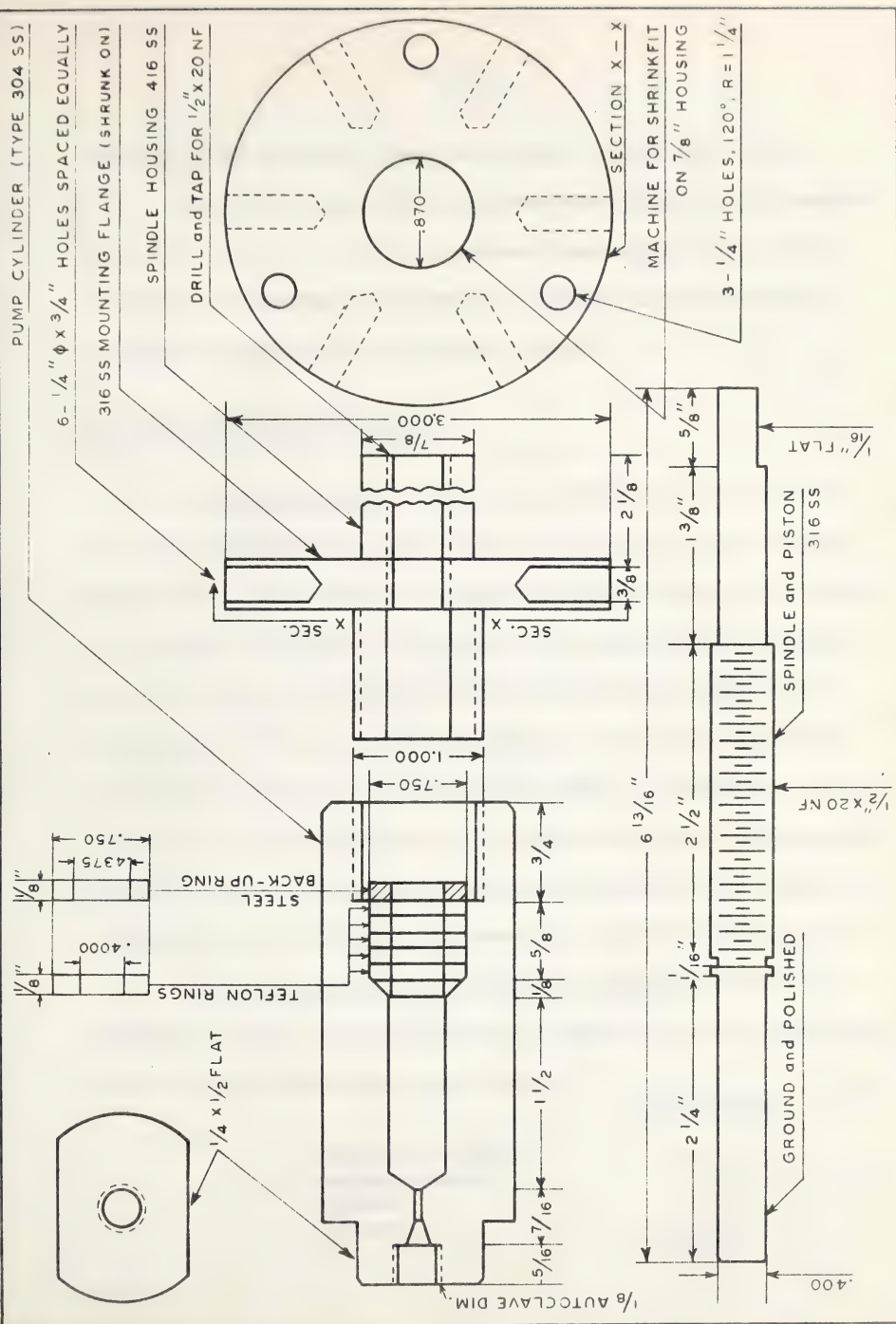


FIG. 3 MICROMETRIC SAMPLE PUMP DETAILS

mercury head from the gauge zero level to the cell level.

The bath liquid used was ethylene glycol. The temperature was controlled using an Aminco bimetallic type thermostat which was connected to a heater and refrigerator assembly by means of an automatic relay.

(2) Experimental Procedures

(a) Cell assembly:- Prior to installing the equipment for this investigation, the cell was dismantled and cleaned thoroughly. Some mercuric sulphide had settled on the window of the cell and great difficulty was experienced in removing it. In view of the difficulties that had been experienced previously⁽¹⁵⁸⁾ in the cell assembly, it was not advisable to take the windows out of the cell body for cleaning. After many unsuccessful attempts with several solvents it was found that an equimolal mixture of ammonium hydroxide and ammonium sulphide was an effective cleanser for removing the deposits.

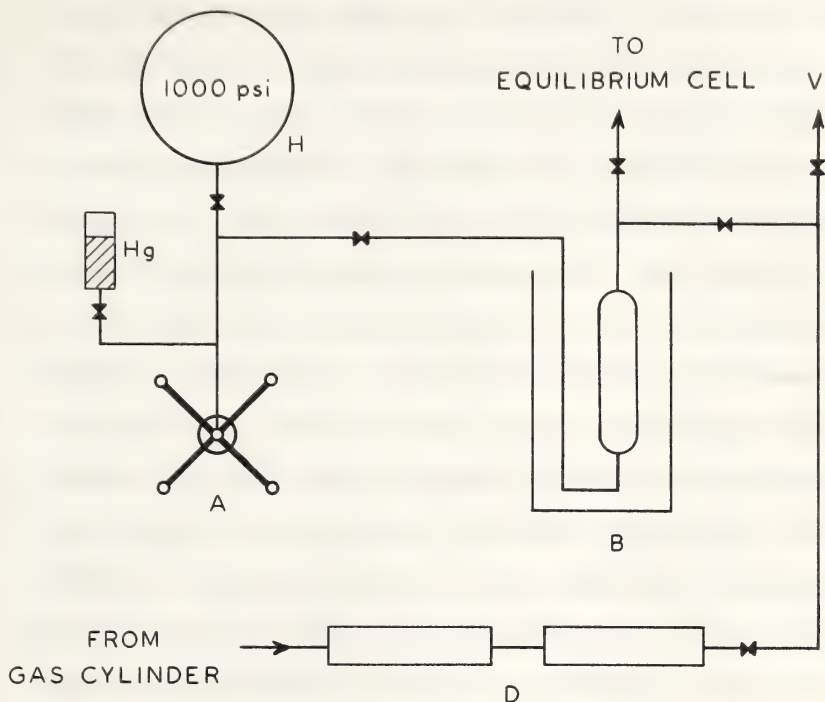
(b) Preparation of experimental mixture:- Recently a natural gas well in the Province of Alberta has been discovered which has the following composition:

	<u>% by Volume</u>
Hydrogen Sulphide	68.00
Carbon Dioxide	9.36
Methane	21.64
Nitrogen	<u>1.00</u>
	100.00

It was decided to study the phase behaviour of a quaternary having the above composition. Mixing the four gases in a proportion close to the above provided great difficulty. Initially, an attempt was made to mix the four gases in a separate windowed cell, but great difficulty was experienced during its transfer to the main cell. It was therefore decided to design a convenient mobile unit to make the samples of a desired composition.

A 300 ml. stainless steel bomb rated at 1,000 psi was used. The top of this bomb could be connected to the sample port of the main cell assembly. The bottom of the bomb was connected through a T to a Ruska displacement pump of 250 ml. capacity and to two driers in series. The driers were filled with anhydrous calcium chloride and Drierite. The calcium chloride drier was connected to the cylinder of the gas that was to be injected in the cell. A Heise pressure gauge rated up to 1,000 psi was used to measure the pressure in the bomb. The bomb was immersed in a constant temperature bath. A mercury thermometer was used to measure the temperatures. Mercury was used as the confining liquid. The schematic arrangement of the unit is shown in figure 4.

All gases were taken in at 100°F. The volume of each gas required to make the desired composition and the corres-



A - DISPLACEMENT PUMP
 B - BOMB AND BATH
 D - DRIERS
 H - HEISE GAUGE
 Hg - MERCURY HOLDER
 V - VACUUM LINE

FIG. 4

SCHEMATIC DIAGRAM OF APPARATUS FOR THE
 PREPARATION OF SAMPLES

ponding pressure were previously calculated. Initially, the cell, the bomb, and the adjoining lines were evacuated and filled with mercury. The valve connecting the cell assembly to the bomb was closed. The driers were purged with hydrogen sulphide gas. The desired volume of the gas was sucked in the bomb at the known pressure and temperature. The bomb was then isolated from the drier unit and the gas in the bomb was pushed into the cell by actuating the mercury displacement pump. In the same way, carbon dioxide, methane, and nitrogen were introduced in this order. Hydrogen sulphide was introduced first because it was the major component and because it has the lowest vapour pressure of all the components. Carbon dioxide, which has the next higher vapour pressure over the H_2S was immediately followed to avoid its liquifaction in the lines at higher pressures. Nitrogen, since it was the trace component was introduced last.

After the hydrogen sulphide gas had been admitted great caution was exercised not to add an excess of any other component. Minor deficiencies in the amounts of carbon dioxide, methane, and nitrogen were made up in this order. Intermediate analyses of the cell mixture when it existed in a single phase were carried out to determine how far the composition was from the desired. The method of analysis is presented later.

An attempt was made to use the available compressibility factor charts to calculate the amounts required and the corresponding conditions of each gas to make the desired mixture. The results of these calculations were not found to be correct and thus trial and error was the only method available to mix the gases in the right proportion.

Once the mixture of a composition close to the desired had been made, the valve connecting the cell to the sample pump was firmly closed. The data were taken in two parts. Firstly, only the two phase envelope of the system was determined by measuring the amount of liquid present at the known pressure and temperature of the equilibrium. Regular checks were made to see if any appreciable change had occurred in the composition of the cell mixture. The composition was found to remain constant all through this part of the investigation. The second part consisted in analysing the two phases at equilibrium to calculate the equilibrium ratios for each component. Data obtained in this part of the investigation provided a check on the data of part one.

The temperature was recorded and maintained constant all the time as equilibrium was being attained by spraying the liquid and mercury through the bottom valve. This could be taken as the point at which further spraying of

mercury caused no subsequent change in the pressure. The equilibrium pressure was recorded. The volumes of liquid and gas present were measured by noting the volumes indicated on the double acting pump when mercury, liquid, and the piston pin end were on the reference level in the window. This procedure was repeated at other pressures and temperatures.

Samples of gas and liquid were removed through the sample pump and carefully expanded to atmospheric conditions in a gas-burette for chromatographic analysis. The size of the liquid to gas samples withdrawn was in proportion to the amounts present in the cell. This helped in keeping the composition of the cell mixture reasonably constant. A slight change did occur in the overall composition of the cell mixture but this would not affect the K-values appreciably. The sampling procedure has been reported previously⁽⁶⁰⁾.

As the sample was being removed from the cell, mercury was added to it at the same volumetric rate. Pressure was thus maintained constant and the equilibrium was not disturbed.

The dew point was noted by the first appearance of liquid. This was further checked by reversing the procedure and noting the disappearance of the liquid. Extrapolation of the plot of percent liquid versus pressure gave the bubble

point pressure. Near the critical conditions neither the dew point nor the bubble point was apparent, and much longer time was required to achieve equilibrium.

(3) Materials

Mercury was used as the displacement liquid. Since the combination of mercury and hydrogen sulphide, in the presence of moisture caused almost instantaneous blackening of mercury, considerable care was taken to insure that pure mercury was used. The procedure for the purification of mercury has been reported previously (158).

All gases were dried before introducing them into the cell. The gases used were all over 99% pure as indicated upon a chromatographic analysis and no further purification was necessary. Carbon dioxide and nitrogen were obtained from Liquid Carbonic. Matheson supplied the C.P. grade hydrogen sulphide and pure methane was obtained from the Phillips Petroleum Company.

(4) Analysis

The vapour and liquid samples were analysed using a Burrel K₂ Kromo-tog. Two columns were used. A column packed with ansul ether on 25% silocel separated methane, nitrogen,

and air as one component, carbon dioxide, and hydrogen sulphide. A molecular sieve type 13-X column separated oxygen, nitrogen and methane. Molecular sieves block carbon dioxide and hydrogen sulphide and are temporarily degenerated upon prolonged exposure to these gases. A constant check on the calibration revealed that it had not changed due to the slight amounts of the acid gases introduced with each sample.

Satisfactory separation was obtained for all components. Pure gases were used for the calibrations. By using 7 samples of different volumes, sample volume could be plotted against the peak heights, satisfactory linear curves were obtained for all components and for both the columns. Four known synthetic mixtures of all the four gases were made in a gas burette and analysed and it was found that for both the columns there is a negligible interaction among the various components. The volumes read from the calibrations always added up to within $\pm 1\%$ of the actual sampler volume. The chromatographic calibrations are presented in figures 14 and 15 of the appendix.

The column conditions were:

I	Column	Ansul ether on 25% silocel
	Column length	7 feet 8 inches
	Carrier gas	Helium at 79.3 ml/min.
	Detector Current	200 mA

Column Temperature 90°F

Sample Size 1.85 ml

II Column Molecular sieve, type 13X

Column Size 8 feet 4 inches

Carrier Gas Helium at 67 ml/min

Detector Current 200 mA

Column Temperature 90.5°F

Sample Size 1.85 ml

The retention times were as follows:

I Column:

Methane, air, and nitrogen 0.75 min.

Carbon dioxide 1.05 min.

Hydrogen sulphide 3.10 min.

II Column:

Oxygen 1.625 min.

Nitrogen 2.375 min.

Methane 4.500 min.

D. EXPERIMENTAL RESULTS

The composition of the system used for this investigation was:

	<u>% by Volume</u>
Hydrogen sulphide	68.04
Carbon dioxide	9.30
Methane	21.70
Nitrogen	<u>0.96</u>
	100.00

The two phase envelope of the system was determined at nine temperatures 35°, 60°, 90°, 120°, 140°, 150°, 160°, 170°, and 180°F. Figures 5 and 6 are plots of the data on pressure versus percent liquid coordinates and with temperature as the parameter. The nine temperatures define the phase envelope adequately. Figure 7 is the two phase envelope for the system on pressure-temperature coordinates showing the lines of constant percent liquid. Figure 7 was obtained by cross plotting the data of Figures 5 and 6. The results are tabulated in tables 6 - 9 of the appendix.

Critical Point

The phenomenon of critical opalescence was observed at 140°F and 1,761 psia. Figure 8 is a photograph of the critical phenomenon taken through a periscope-telescope arrangement.

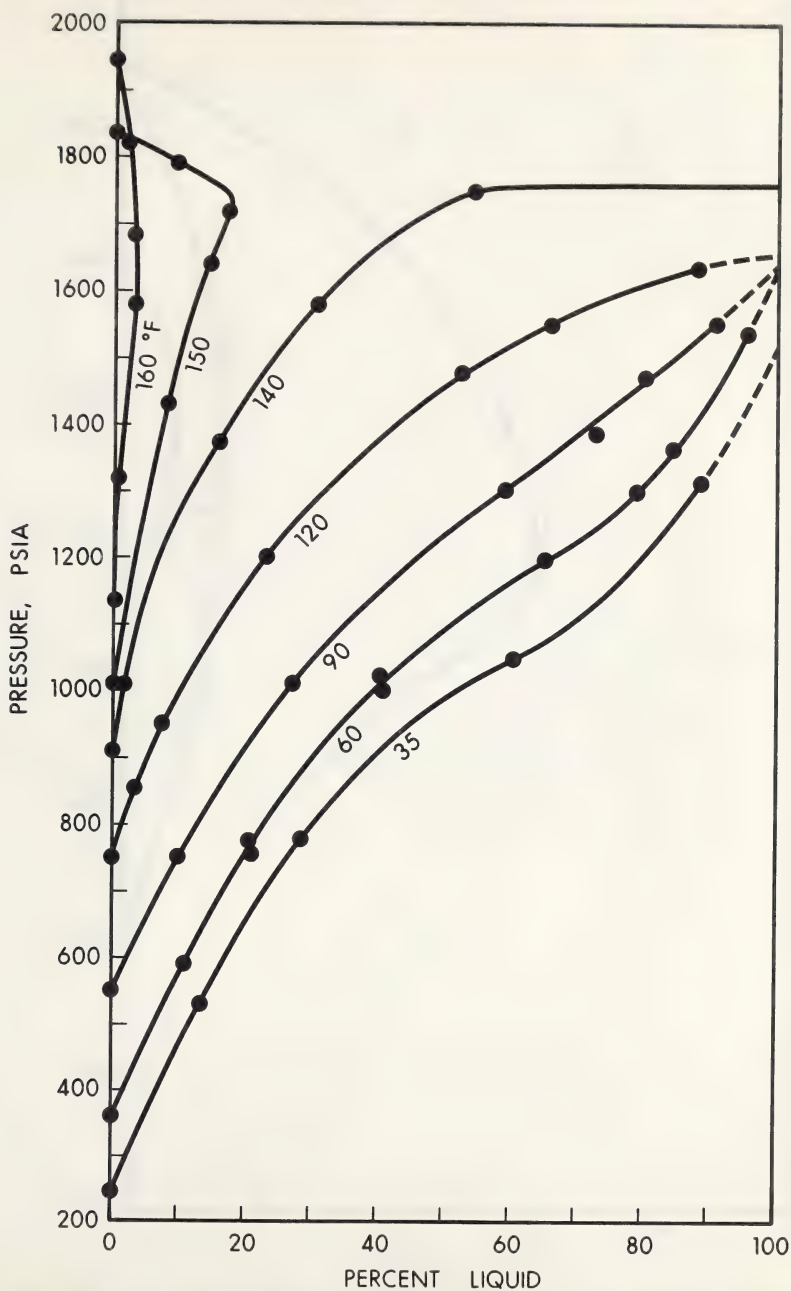


FIG. 5 ISOTHERMS FOR THE $H_2S - CO_2 - CH_4 - N_2$ SYSTEM

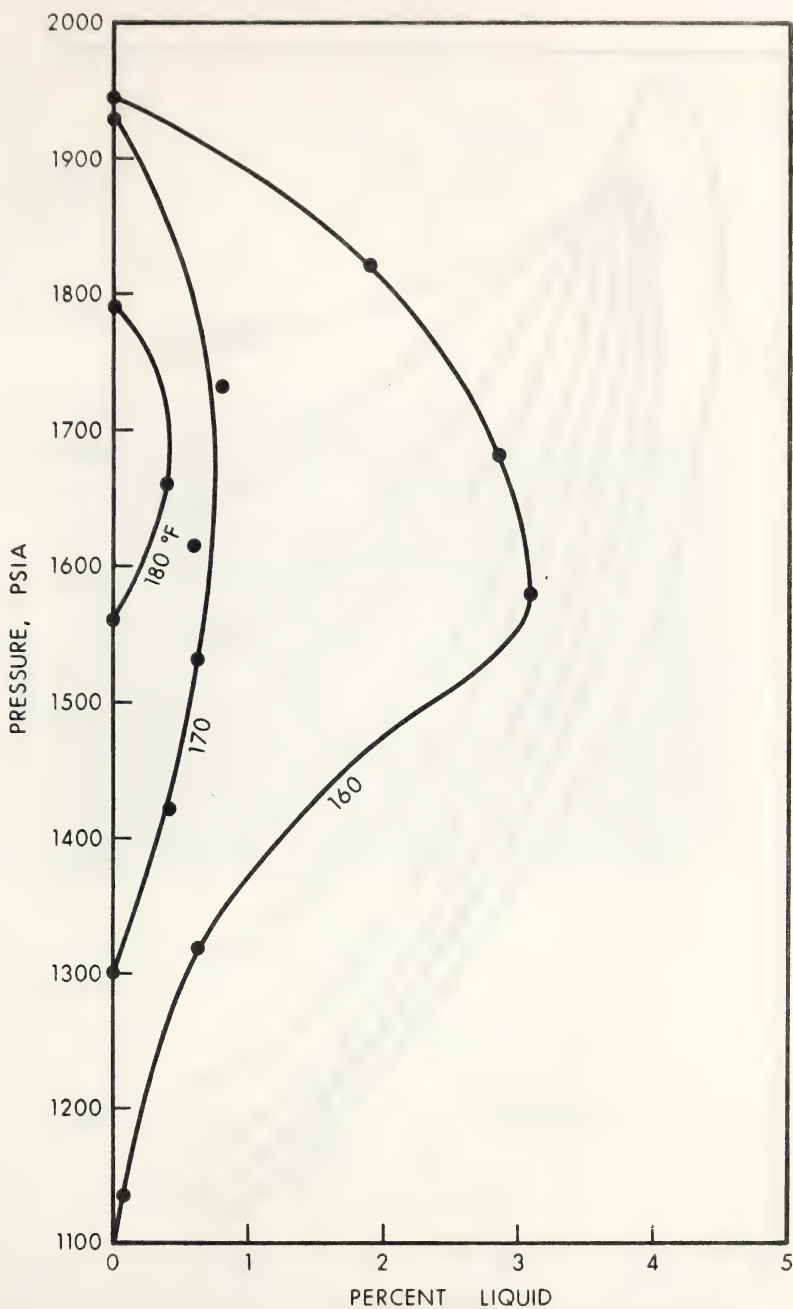


FIG. 6 ISOTHERMS FOR THE $\text{H}_2\text{S} - \text{CO}_2 - \text{CH}_4 - \text{N}_2$ SYSTEM IN THE RETROGRADE REGION

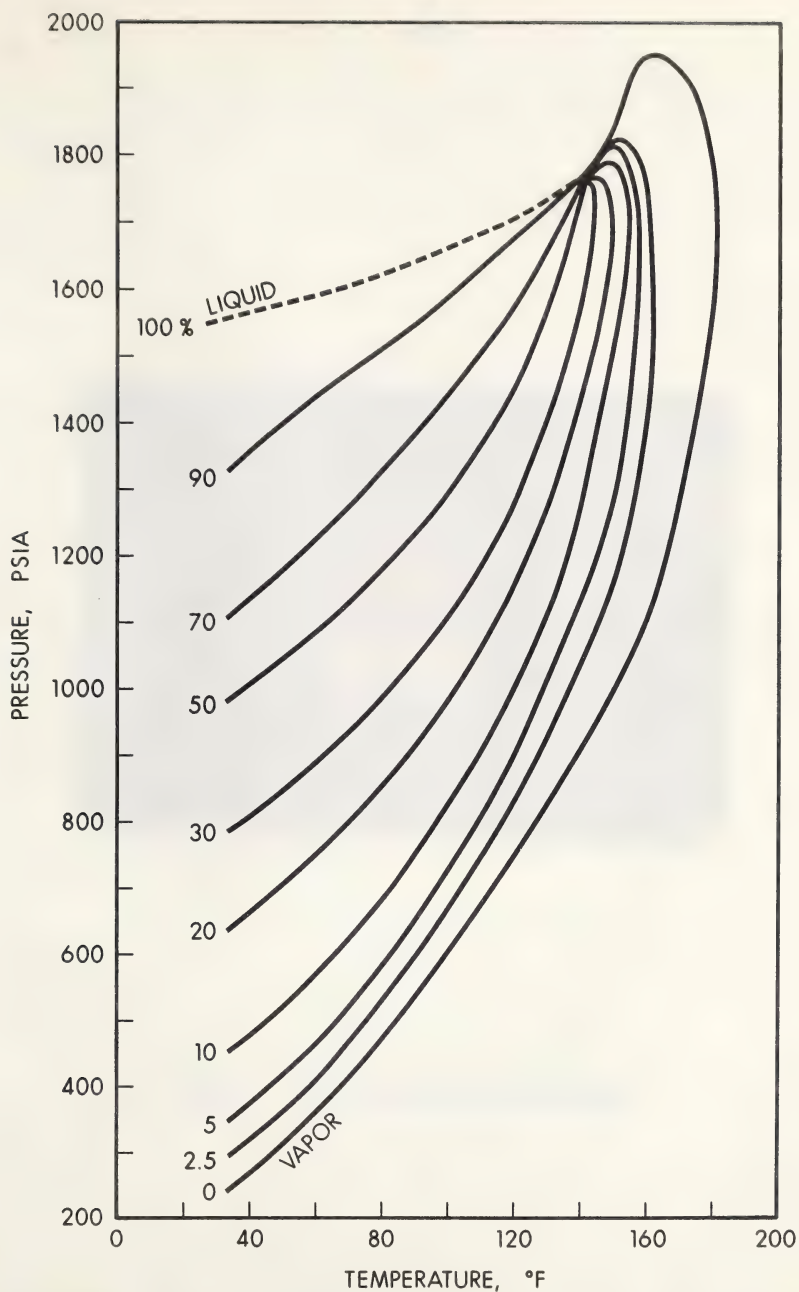


FIG. 7 PHASE ENVELOPE FOR THE $\text{H}_2\text{S} - \text{CO}_2 - \text{CH}_4 - \text{N}_2$ SYSTEM



FIGURE 8 THE CRITICAL OPALESCENCE

The critical phenomena exhibited the following characteristics:

(1) A reddish-orange opalescence was observed with transmitted light.

(2) Reflected light produced a bluish-white colour.

(3) The thickness of the interface between liquid and vapour increased as the critical point was approached by changing the pressure at the critical temperature. The interface was undefined at the critical point.

(4) The opalescence was more intense in the liquid phase when the pressure was reduced from a higher value to the critical pressure. When the critical point was reached by slowly increasing the pressure, the vapour phase exhibited a more intense opalescence.

(5) The opalescence was not observed in the main body of the cell mixture.

(6) The fluid in the immediate vicinity of the piston pin showed a more intense opalescence. Sometimes a very fine spray of liquid rose in a jet toward the piston pin.

(7) The critical point was reproducible within ± 0.5 psia and $\pm 0.2^\circ\text{F}$.

The analysis of the phases was made at only one temperature 120°F. The equilibrium ratios were calculated for methane, carbon dioxide, and hydrogen sulphide. The values for nitrogen were not considered adequately reliable due to the very low proportion of nitrogen present in both the phases. The results are plotted in figure 9 and are tabulated in tables 8 and 9 of the appendix.

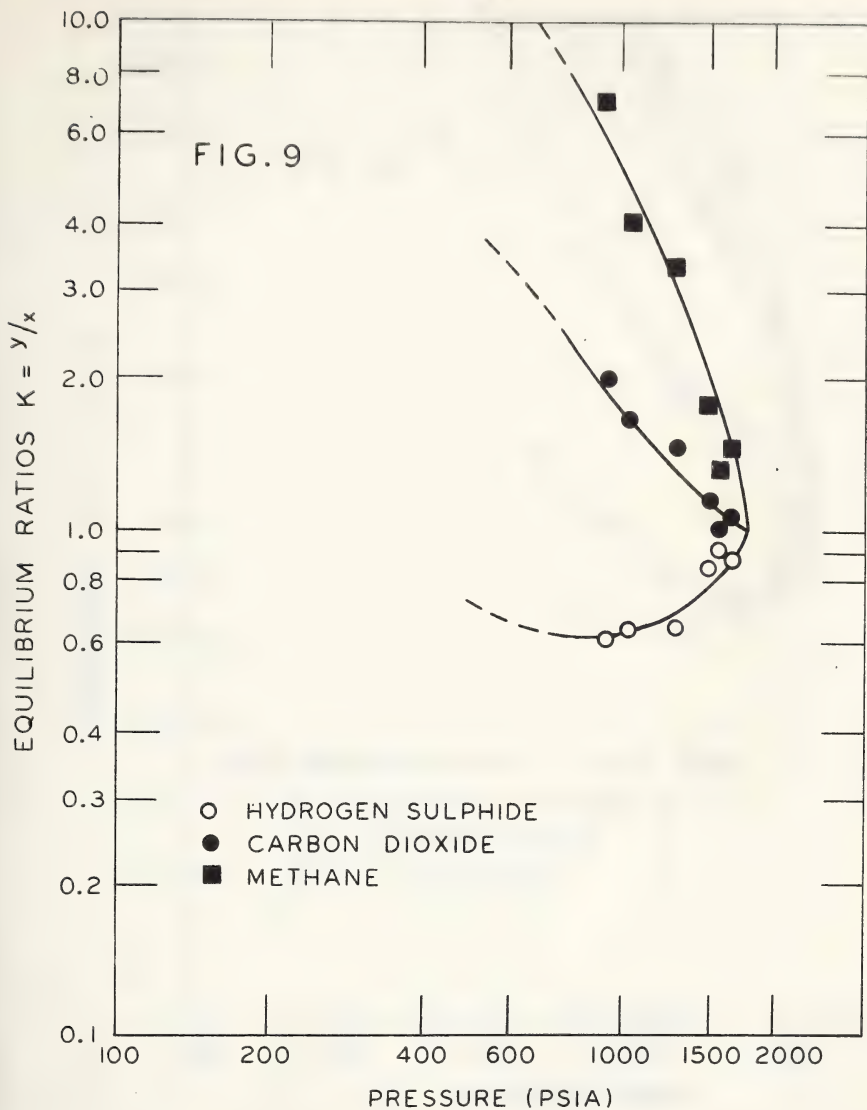
The composition of the cell mixture had changed to the following due to the withdrawal of about 24 samples of vapour and liquid from the cell.

	<u>% by Volume</u>
Hydrogen sulphide	59.18
Carbon dioxide	9.95
Methane	29.66
Nitrogen	<u>1.21</u>
	100.00

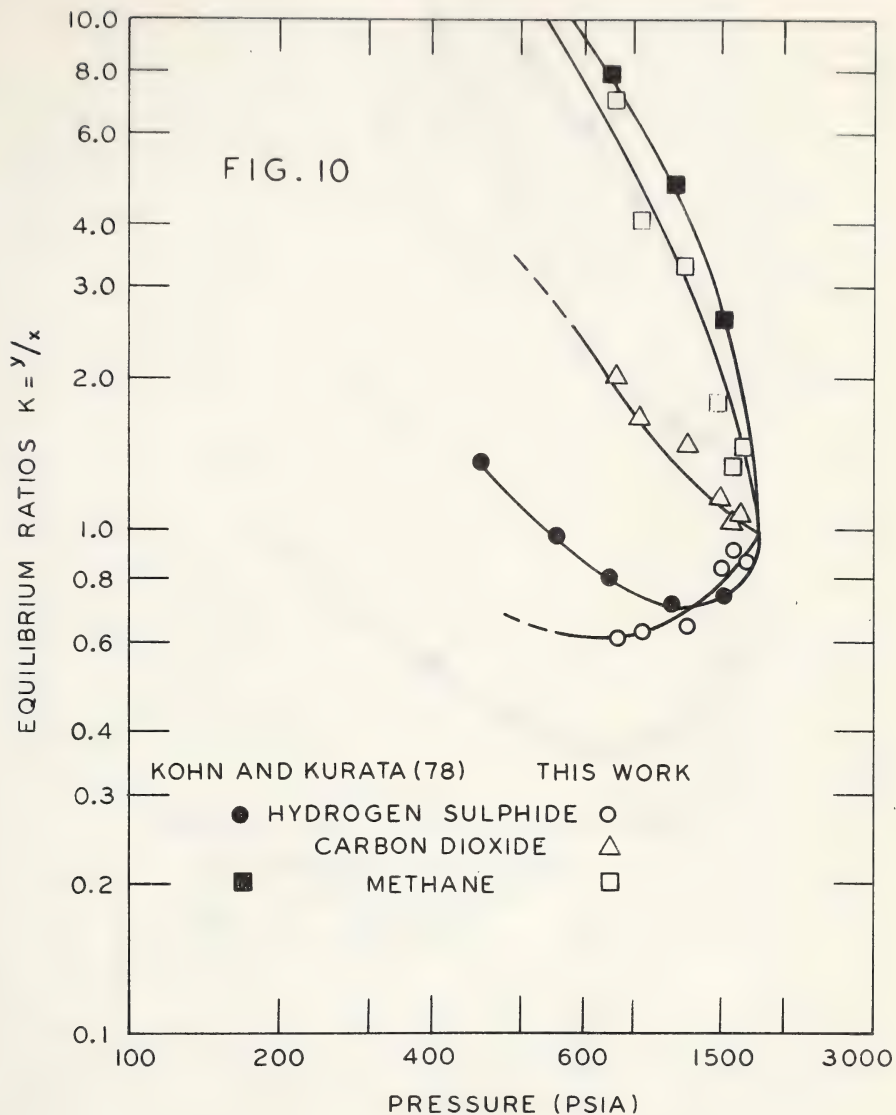
The experimental data were consistent and reproducible.

The k-values obtained during this investigation are compared with the following:

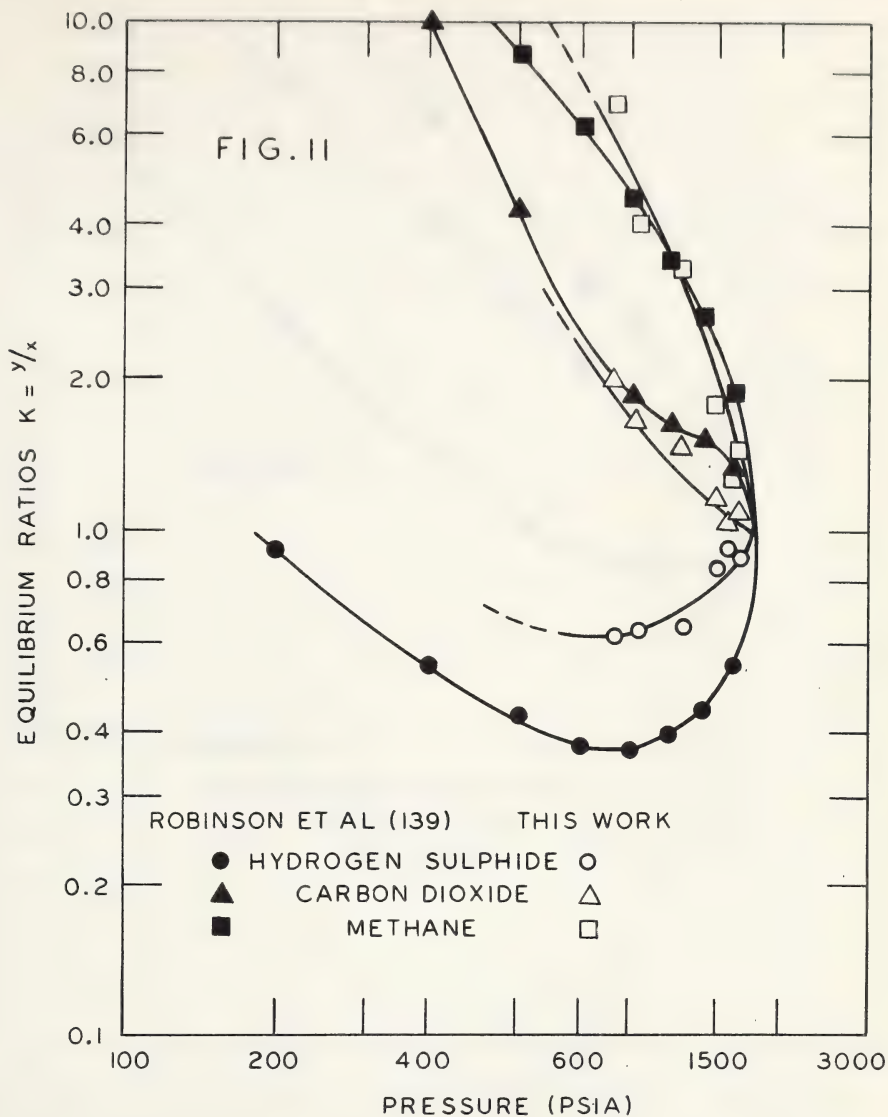
- (1) Data of Kohn and Kurata⁽⁷⁸⁾ at 140°F and for a $P_{CV} = 1,760$ for the system methane hydrogen sulphide. (Fig. 10)
- (2) Data of Robinson et al⁽¹³⁹⁾ for the system methane - carbon dioxide - hydrogen sulphide at 40°F and for $C_1 = 0.14$, $P_{CV} = 1,760$ psia. (Fig. 11)
- (3) NGSMA⁽⁵⁰⁾ values for $P_{CV} = 1,760$ and at 120°F. (Fig. 12).



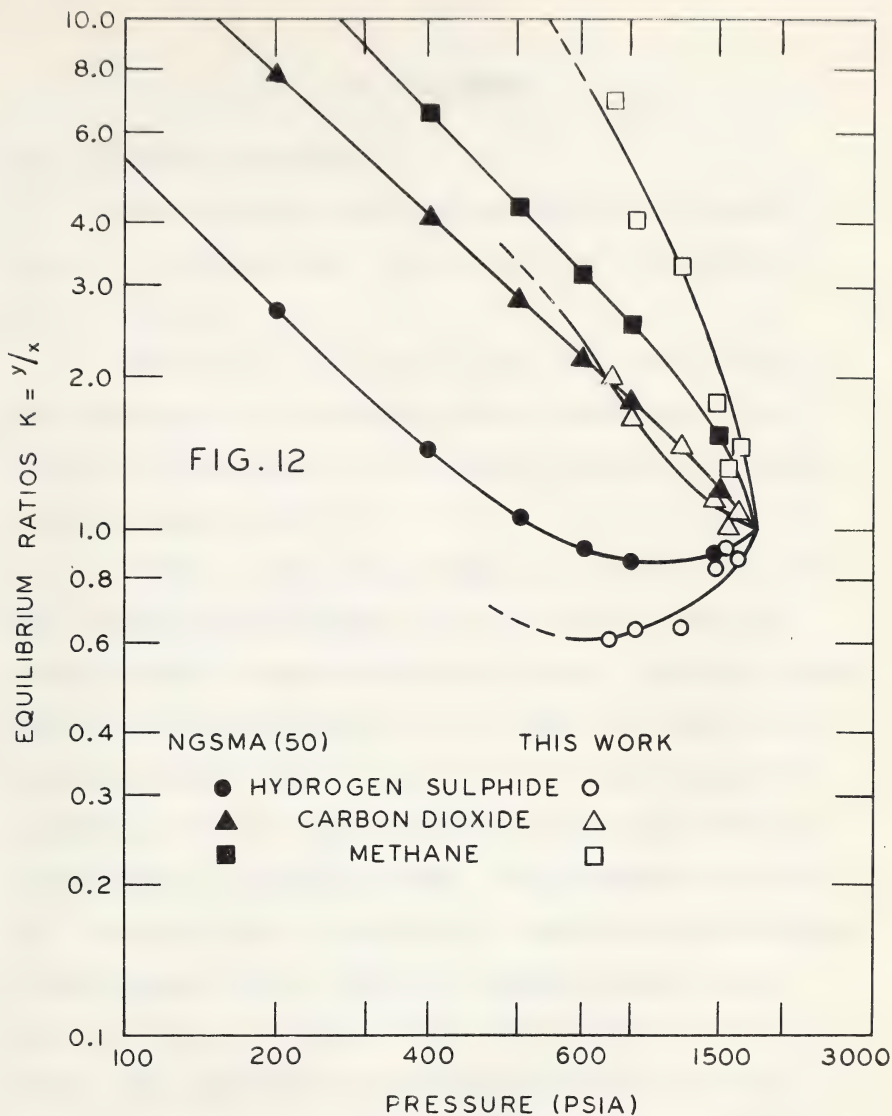
EQUILIBRIUM RATIOS FOR THE H_2S - CO_2 - CH_4 - N_2 SYSTEM AT $120^\circ F$ FOR A CONVERGENCE PRESSURE OF 1761 PSIA



A COMPARISON OF EQUILIBRIUM RATIOS FOR THE $\text{H}_2\text{S}-\text{CO}_2-\text{CH}_4-\text{N}_2$ SYSTEM WITH THOSE PRESENTED BY KOHN & KURATA FOR THE $\text{H}_2\text{S}-\text{CH}_4$ SYSTEM AT 140°F FOR CONVERGENCE PRESSURE OF 1800 PSIA



A COMPARISON OF EQUILIBRIUM RATIOS FOR THE $H_2S-CO_2-CH_4-N_2$ SYSTEM WITH THOSE PRESENTED BY ROBINSON ET AL FOR THE $H_2S-CO_2-CH_4$ SYSTEM AT $40^\circ F$, $C = 0.14$, AND FOR A CONVERGENCE PRESSURE OF 1760 PSIA



A COMPARISON OF EQUILIBRIUM RATIOS FOR THE $H_2S-CO_2-CH_4-N_2$ SYSTEM WITH THOSE PRESENTED IN NGSMA AT $120^\circ F$ FOR A CONVERGENCE PRESSURE OF 1760 PSIA

E. DISCUSSION

(1) Experimental Apparatus

The equilibrium cell was used for a multi-component system for the first time. It was found to be satisfactory for the purpose.

The vertical positioning of the sample pump offered some advantages. It is adequate to have just one port for injecting any component in the cell and also for the sampling of phases from the cell.

A change in the piston design is suggested after this work. In the present design, the total volume of the cell mixture cannot be viewed through the window. The fluid trapped between the bottom of piston (in its lowest position) and the top of the window cannot be seen. It was thus not possible to make any volumetric measurements when very high percentage (above 90%) of liquid was present. It is therefore suggested that instead of the 1/8" diameter pin constructed at the bottom of the piston, a rod of 3/8" o.d. (diameter of the passage connecting the two sections of the cell) be built in the piston. The length of this rod should be such that it can be seen near the top of the window when the piston is in

its lowest position. The rod can then be tapered into a pin that ends at the centre of the window. This will avoid the possibility of liquid drops of any appreciable volume sticking to the tip of the piston.

(2) Discussion of Results

(a) Two phase envelope:- A large retrograde condensation region is apparent from the phase diagram for the system shown in Figure 7. The extrapolated constant percent liquid lines of Figure 7 also appear to converge at the observed critical point at 140°F and 1,761 psi.

Since it was not possible to measure the volumes of phases correctly when more than 90% liquid was present, a certain amount of uncertainty exists at 60°, 90°, and 120°F for lines of percent liquid higher than 90%. This region is shown dotted on the phase envelope of Figure 7.

(b) Critical point:- The critical phenomena observed during the course of this investigation was similar to the one reported earlier by Travers and Usher⁽¹⁷⁷⁾ and Young⁽¹⁹⁵⁾. Their finding that "the opalescence is confined to that phase which is decreasing in volume through movement of the dividing

surface, or at least is most intense in that phase" is confirmed.

There may have been some temperature gradients present between the piston pin and the main body of the fluid. This might be responsible for the unsteady fountain-like stream of droplets striking the piston point as seen in figure 8.

It was not possible to observe the critical opalescence throughout the mixture because the two barrels of the double acting pump are not of exactly the same size; the little change of pressure that occurred when the position of mixture in the cell was changed disturbed the critical conditions appreciably.

(c) Equilibrium ratios:- The equilibrium ratios were determined at one temperature only. The composition of the mixture had changed slightly due to the sampling of phases, but, it should not affect the K-values appreciably.

In order to compare the results of this investigation with those published elsewhere on similar systems, convergence pressure was the only parameter to account for the effect of composition. Comparisons were made with the values of Kohn and Kurata⁽⁷⁸⁾ at $P_{CV} = 1800$ psia and of Robinson et al⁽¹³⁹⁾ and NGSMA⁽⁵⁰⁾ at $P_{CV} = 1760$ psia. Convergence pressure for this system appears to be the same as the critical pressure.

The methane K-values obtained in this investigation are slightly lower than the values reported by Kohn and Kurata⁽⁷⁸⁾ at 140°F for the system methane - hydrogen sulphide. The hydrogen sulphide K-values cross at 1,300 psia. The values of Kohn and Kurata are higher for pressure less than 1,300 psia but are lower than the values of this investigation for pressures above 1,300 psia.

The methane K-values reported by Robinson et al⁽¹³⁹⁾ compare well with the values obtained in this investigation. The curves of figure 11 cross at 1,300 psia. The values of Robinson et al are lower than the methane K-values presented here for pressure less than 1,300 psi and are higher above this pressure.

The carbon dioxide K-values reported by Robinson et al are higher than the values obtained in this work but the difference between the two is not more than 0.3. The K-values equal each other for pressures less than 1,000 psia. The hydrogen sulphide K-values are always lower than the values obtained during this work.

The methane K-values interpolated from the NGSMA Engineering Data Book for a convergence pressure of 1,760 psia and at 120°F are much lower than the values of this investigation.

The carbon dioxide values compare well. The curves of figure 12 cross at 880 psia. The NGSMA values are slightly higher than the values obtained in this investigation for pressures above 880 psia and lower for pressures below this.

The NGSMA values for hydrogen sulphide are always higher than the values presented here.

F. CONCLUSIONS

(1) The two phase envelope of a quaternary natural gas system was established by measuring percent liquid present for different pressures at nine temperatures: 35°, 60°, 90°, 120°, 140°, 150°, 160°, 170°, and 180°F.

(2) Critical opalescence was observed and the phenomenon was compared with the observations of other workers.

(3) The equilibrium ratios for hydrogen sulphide, carbon dioxide and methane were calculated at 120°F and compared with the values available from the literature on similar systems.

(4) Due to the scanty data available on identical systems, the results of this investigation could only be compared with the data reported on $\text{H}_2\text{S}-\text{CH}_4$ and $\text{H}_2\text{S}-\text{CO}_2-\text{CH}_4$ systems. It is not possible to make any general statements, but, comparison of the results serves to indicate that the convergence pressure is a potential and convenient parameter to account for the effects of composition on equilibrium ratios.

(5) The existing equipment was modified and used for the first time to study the phase behaviour of a multicomponent system. It is suggested that the piston design be modified.

NOMENCLATURE

f	fugacity of a component
\bar{f}	fugacity of a component in a mixture
f_i^L	fugacity of the i^{th} component in the pure liquid state
f_i^V	fugacity of the i^{th} component in the pure vapour state
n	number of components in the system
K	equilibrium ratio
P	total pressure of the system
p_v	vapour pressure of a component at the temperature of the equilibrium
p	partial pressure of a component at the temperature and pressure of the equilibrium
P_{cv}	convergence pressure
v	molal volume of vapour
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
γ	activity coefficient

Subscripts

i	component i
L	liquid phase
v	vapour phase

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Appendix I

TABULATIONS OF EXPERIMENTAL RESULTS

Table 6

TWO PHASE ENVELOPE FOR THE QUATERNARY NATURAL GAS SYSTEM

<u>Temperature °F</u>	<u>Pressure psia</u>	<u>Volume of the System, ml</u>	<u>Volume of Liquid ml</u>	<u>Percent Liquid</u>
35	246		0.00	0.00
	528	43.64	5.88	13.47
	778	23.82	6.97	28.42
	1048	12.83	7.73	60.30
	1315	9.57	8.47	88.50
60	360		0.00	0.00
	590	49.47	5.43	10.97
	775			20.54
	755	30.85	6.53	21.00
	1000			40.63
	1024	17.50	7.92	45.25
	1197			65.00
	1300	11.82	9.31	78.76
	1365	10.87	9.16	84.26
	1540	9.42	8.99	95.45
90	550		0.00	0.00
	750	48.65	4.78	9.82
	1011	25.44	6.90	27.12
	1302	15.00	8.86	59.06
	1386	13.15	9.56	72.70
	1472	12.32	10.11	80.07
	1552	12.02	10.91	90.76
120	750		0.0	0.00
	855	58.50	2.00	3.42
	950	45.88	3.44	7.50
	1200	26.91	6.18	22.96
	1477	16.94	8.86	52.30
	1551	14.88	9.79	65.80
	1637	13.27	11.67	87.94

Table 6 (Continued)

<u>Temperature</u> <u>°F</u>	<u>Pressure</u> <u>psia</u>	<u>Volume of the</u> <u>System, ml</u>	<u>Volume of</u> <u>Liquid ml</u>	<u>Percent</u> <u>Liquid</u>
140	910		0.00	0.00
	1011	53.41	0.93	1.75
	1372	25.61	4.03	15.73
	1578	19.55	5.98	30.60
	1748	15.46	8.37	54.14
	1761		Critical Point	
150	1010		0.00	0.00
	1430	27.30	2.20	8.06
	1789	17.75	1.65	9.29
	1640	19.94	2.89	14.50
	1718	19.13	3.28	17.14
	1835		0.00	0.00
160	1135	48.97	0.05	0.10
	1318	36.70	0.23	0.63
	1821	18.93	0.35	1.90
	1682	21.63	0.60	2.85
	1579	24.26	0.75	3.09
	1945		0.00	0.00
170	1300		0.00	0.00
	1421	35.77	0.15	0.42
	1615	28.21	0.17	0.60
	1532	31.24	0.20	0.64
	1732	24.76	0.21	0.81
	1930		0.00	0.00
180	1560		0.00	0.00
	1660	24.1	0.10	0.40
	1790		0.00	0.00

Table 7

TWO PHASE ENVELOPE FOR THE QUATERNARY NATURAL GAS SYSTEM

Temperature °F Percent Liquid	Pressure, psia							
	35	60	90	120	140	150	160	170 180
0.00	250	360	540	750	910	1010	1090	1300 1560
2.50	302	415	602	833	1046	1835	1945	1930 1790
5.00	356	467	651	899	1141	1155	1552	1824 1749
10.00	462	570	748	1000	1266	1285	1812	1510 1786
20.00	647	750	915	1157	1440			
30.00	795	895	1046	1280	1572			
40.00	906	1005	1146	1376	1668			
50.00	988	1090	1232	1456	1731			
60.00	1050	1164	1310	1521	1760			
70.00	1112	1226	1385	1572	1760.1			
80.00	1205	1312	1465	1612	1760.4			
90.00	1335	1441	1548	1641	1760.7			
100.00	1520	1640	1640	1657	1761			

Table 8

VAPOR-LIQUID EQUILIBRIUM DATA FOR THE QUATERNARY
NATURAL GAS SYSTEM AT 120°F

Pressure <u>psia</u>	<u>Component</u>	Composition, Mole Fraction	
		<u>Vapour</u>	<u>Liquid</u>
926	H ₂ S	0.5562	0.9014
	CO ₂	0.1000	0.0498
	CH ₄	0.3300	0.0474
	N ₂	0.0138	0.0014
1030	H ₂ S	0.5400	0.8481
	CO ₂	0.1150	0.0695
	CH ₄	0.3310	0.0808
	N ₂	0.0140	0.0016
1265	H ₂ S	0.5429	0.8342
	CO ₂	0.1048	0.0715
	CH ₄	0.3382	0.0924
	N ₂	0.0141	0.0019
1483	H ₂ S	0.6753	0.7931
	CO ₂	0.0904	0.0782
	CH ₄	0.2288	0.1278
	N ₂	0.0055	0.0009
1568	H ₂ S	0.7005	0.7627
	CO ₂	0.0856	0.0844
	CH ₄	0.2023	0.1509
	N ₂	0.0116	0.0020
1639	H ₂ S	0.6666	0.7543
	CO ₂	0.0929	0.0862
	CH ₄	0.2308	0.1582
	N ₂	0.0097	0.0013

Table 9

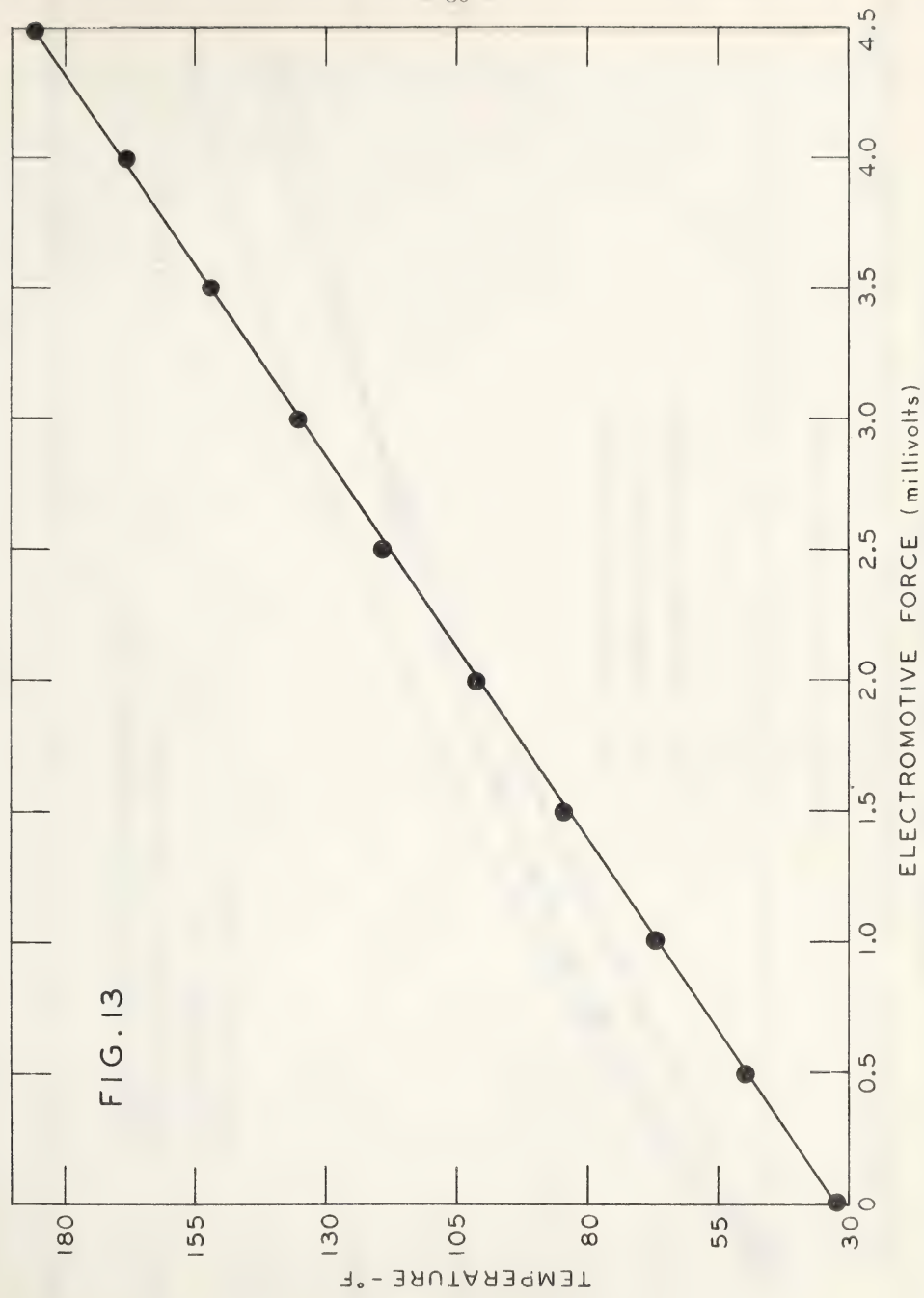
EQUILIBRIUM RATIOS FOR THE QUATERNARY NATURAL
GAS SYSTEM AT 120°F

Pressure psia	Equilibrium Ratios			
	<u>H₂S</u>	<u>CO₂</u>	<u>CH₄</u>	<u>N₂</u>
926	0.617	2.008	6.962	9.857
1030	0.637	1.655	4.097	8.750
1265	0.651	1.467	3.660	7.421
1433	0.851	1.156	1.790	6.111
1568	0.918	1.014	1.341	5.800
1639	0.834	1.078	1.459	7.462

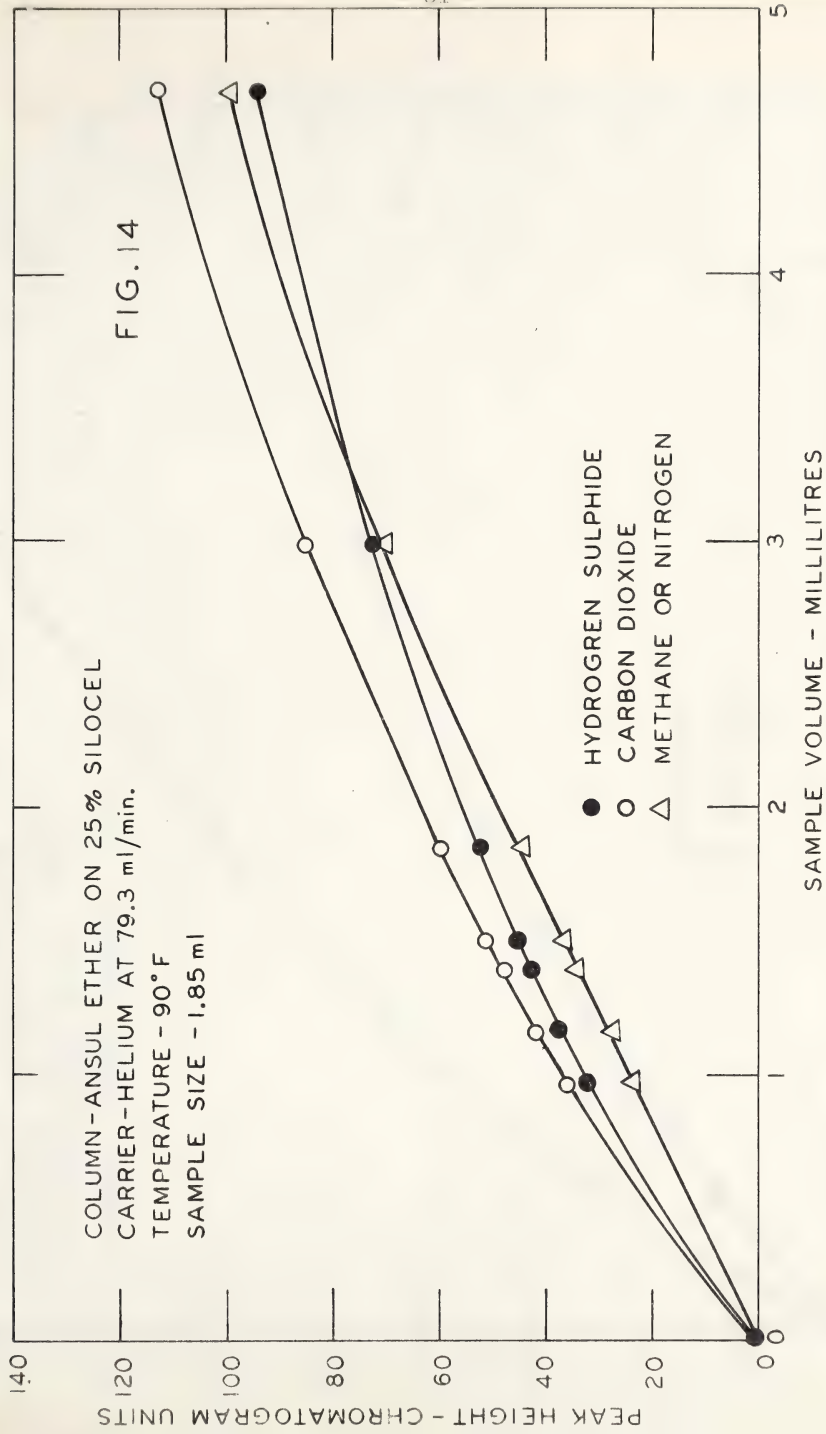
Appendix II

CALIBRATIONS

FIG. 13



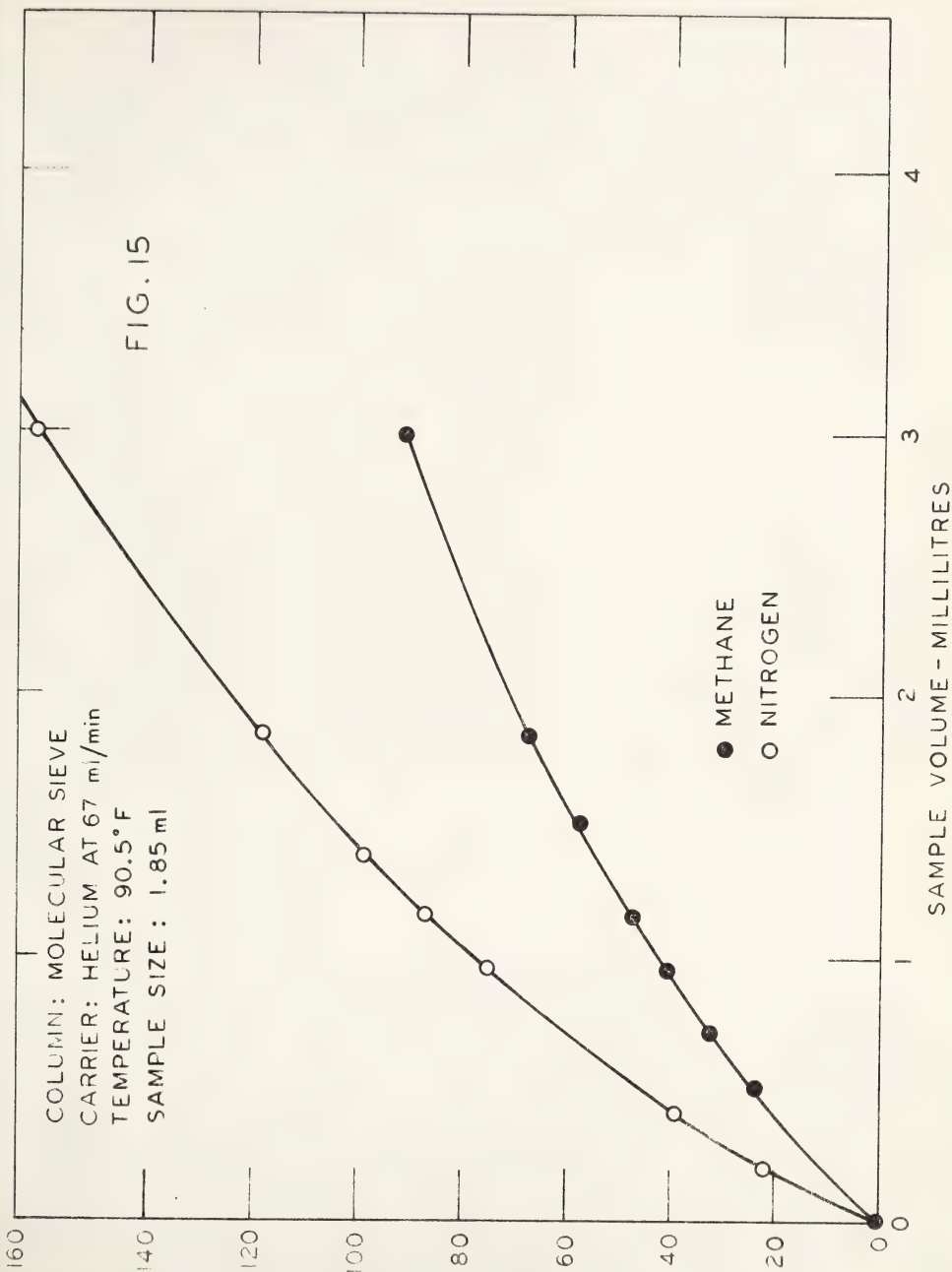
IRON-CONSTAN THERMOCOUPLE CALIBRATION



CALIBRATION OF CHROMATOGRAPH FOR HYDROGEN SULPHIDE-CARBON-DIOXIDE-METHANE-NITROGEN MIXTURES

FIG. 15

COLUMN: MOLECULAR SIEVE
 CARRIER: HELIUM AT 67 ml/min
 TEMPERATURE: 90.5°F
 SAMPLE SIZE: 1.85 ml



CALIBRATION OF CHROMATOGRAPH FOR METHANE-NITROGEN MIXTURES

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